7th International Symposium on Materials for Energy Storage and Conversion

&

11th International Conference on Nanomaterials and Advanced Energy Storage System

Book of Abstracts/Proceedings

17-21 July 2023
Muğla Sıtkı Koçman University

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mESC-IS 2023

The Seventh International Symposium on Materials for Energy Storage and Conversion

INESS 2023

The Eleventh International Conference on Nanomaterials and Advanced Energy Storage System

Edited by
Ezgi Onur Şahin

17-21 July 2023
Mugla Sıtkı Koçman University

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Participants in the Joint Event- mESC-IS &INESS 2023

Preface

The 7th International Symposium on Materials for Energy Storage and Conversion ,**mESC-IS 23** was held jointly with **INESS 23**, i.e. 11 th International Conference on Nanomaterials and Advanced Energy storage system. The joint event has taken place ın Mugla Sıtkı Kocman University from 17th to 21 July 2023. Three circulars were distributed starting from January to May 2023 and submissions were invited in four major activity areas, i) batteries and supercapacitors, ii) fuel/electrolytic cells, and iii) hydrogen for energy storage and transport. The joint event also had special sessions on iv) research methods in batteries and fuel cells and v) prototyping, life assessment and battery recycling.

A total of 168papers were accepted for the symposium. Of these 30 were in plenary sessions and 96 were in parallel sessions. Poster session was held on Thursday Afternoon in which a total of 69 posters were presented. Based on the evaluation of session chairs and senior member of mESC-IS&INESS community , the best poster awards were granted to Yiğit Akbaş-ÖzgürDarıcıoğlu (*Middle East Technical University),* Maksat Karlykan *(Nazarbayev University*) Vitalii Shevchenko (*Moscow State University) and* Zeynep Başaran Yilmaz (*Gebze Technical University*)

Selected papers from this symposium will be published as a special issue "Advances in Materials for Energy Storage and Conversions" in Materials Research Bulletin

This joint event was made possible with the generous support of several institutions. We, ackowledge the support of Mugla Sıtkı Koçman University hosting this event and provision of the facilities which made this event possible. The support of TUBITAK through programmes 2223-B and 2237-A is also gratefully acknowledged. Contributions from IRN-FACES added an additional depth to this symposium and we thank Dr. Fermin Cuevas making this participation possible. We also acknowledge the support of METU, in particular Professor Y. Eren Kalay.

We extend our sincere appreciation to the Provost of Nazarbayev University, Professor Ilesanmi Adesida, for his invaluable support. We also express our gratitude to the Ministry of Digital Development, Innovation and Aerospace Industry, Kazakhstan, for their generous support provided through the targeted research program #51763/PCF-MCROAP PK-19 "New materials and devices for defense and aerospace applications".

We would like to thank Professors Rick Ubic and Won Park for the opportunity to publish the selected papers from this symposium as a special issue in Materials Research Bulletin.

Finally we thank all session chairs, authors and participants for their valuable contributions.

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Zhumabay Bakenov

Tayfur Özturk

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PROGRAM

mESC-IS 2023
7th International Symposium on Materials for Energy Storage and Conversion

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16th July 2023 (Sunday)

19:30 21:00	**Welcome reception** Meet at Akyaka Quay 19:30 Boat Tour from Akyaka to Cınar Beach

17Th July 2023 (Monday)

09:00 18:30	**Registration**
09:30 10:00	**Opening Session** (open to public)
	Berke Pişkin, Local Orginizing Committe
	Tayfur Öztürk, Co-chair mESC-IS
	Zhumabay Bakenov, Co- chair INESS
	Turhan Kaçar, Rector, Mugla Sıtkı Koçman University
10:00 10:30	The NLV: A new ultra-fast charging technology for lithium ion batteries (online) S- **Rachid Yazami**
	Chair: Zhumabay Bakenov **Hall B**
10:30 11:00	Materials and Design for Solid State Batteries M-34 **Cengiz Ozkan**
11:00 11:30	Connecting solar- and wind electricity to the grid drastically increase interest in aqueous batteries M-15 **Dag Noréus**
11:30 12:00	Impedance and noise as non-invasive methods for lithium metal anodes M-36 **Burak Ulgut**
	Coffee Break

177h July 2023 (Monday)

	Chair:**Aligül Büyükaksoy** **Hall C**	Chair: **Mihri Özkan** **Hall B**	Chair:**Batukhan Tatykayev** **Hall D**
12:20 12:45	Development of bolt-microtubular solid oxide fuel cells **M-147** Sezer Onbilgin, Tolga Altan, Cigdem Timurkutluk ve **Bora Timurkutluk**	The formation of residual Li compounds on Ni-rich NCM cathodes and their effect on the electrochemical performance in LPSCl-based ASSBs M-80 **Burak Aktekin**, Anja Henss and Jürgen Janek	Utilization of waste aluminum for hydrogen production and material recycling M-119 **Marius Urbonavicius,** Sarunas Varnagiris, Darius Milcius, Ainars Knoks and Peteris Lesnicenoks
12:45 13:05	Impact of spin coating rates on the surface chemistry and electrochemical performance evolution of (La,Ca)CoO3 solid oxide cell electrodes M-122 Mehmet Sezer , Ali Ahsen and **Aligul Buyukaksoy**	A Novel Approach Enabling Atomic Scale Characterization for Li-on Battery Components probed by Positron Annihilation Lifetime Spectroscopy (PALS) M-23 **Recep Bakar** , Süleyman Koç, Ayşe Yumak Yahşi and Uğur Yahşi	Effect of transition metal salts on the electrocatalytic properties of Ni-foam modified by ‘’Dip and Drying’’ method M-24 Evelina Slavcheva and Elitsa Petkucheva
13:05 13:25	Hysteresis effect reduction in printed and flexible perovskite solar cells with SnO2 quantum dot-based electron transport layers S-33 **Askhat Jumabekov**	The mixed ionic and electronic conductor LLZO solid electrolytes for lithium-ion battery cathodes M-132 **Semih Engün** , A.Uygar Şimşek, Betül Gür and Servet Turan	Machine learning analysis of photoelectrochemical water splitting M-69 **Burcu Oral** , Elif Can Özcan and Ramazan Yıldırım
13:25 13:45	Effect of porosity-graded (La,Sr)FeO3 –(Ce,Sm)O2 electrode layers on the long-term performance of solid oxide electrolysis cell under anodic polarization M-84 **Büşra Günhan** and Aligul Buyukaksoy	Coaxial Fiber-Shaped Highly Flexible Li-ion Battery for Powering Textile Electronics S-32 **Muniraj Vedikuyilazhagan**	Hydrogen processing as a way of producing fine metallic powders M-159 **Zeynep Ege Uysal**, Sertac Altinok, Y. Eren Kalay and Tayfur Ozturk

Lunch Break

	Chair:Bilge Saruhan-Brings Joint Session-II **Hall B**
16:45 17:10	Artificial-intelligence assisted search for best energy-conversion materials S-9 **Sergey V. Levchenko**
17:10 17:35	One-step fabrication of all-in-one flexible nanofibrous lithium-ion battery S-1 **Almagul Mentbayeva**
17:35 18:00	An investigation of the cathode electrolyte interphase (CEI) formation of Ni rich layered materials by Ni ion catalyzation: monolayer CEI formation from an oligomer S-8 **Fu Ming Wang**
18:00 18:30	Breakthrough in enhancement of hole mobility in strained germanium semiconductor leads to emergence of new class of quantum materials S-3 **Maksym Myronov**

	18th July 2023 (Tuesday)
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10:30 11:00	Alkaline electrolyser for green hydrogen production: the nickel-based catalyst and separator M-68 **Gülfeza Kardaş**
11:00 11:30	Operando Monitoring and Insights for Hydrogen Production via Electrolysis M-87 **Begum Yarar Kaplan** , Ahmet Kırlıoğlu, Mohammad Alinezhadfar, Mohammed Ahmed Zabara, Naeimeh Rajabalizadeh Mojarrad, Bilal Sayyed Said
11:30 12:00	Materials for Fuel Cells and Electrolysis Technologies: Challenges and Perspectives M-10 **Selmiye Alkan Gürsel**
12:00	Coffee Break

	Chair: Ramiz Gültekin Akay **Hall C**	**Chair: Ali Sarı** **Hall B**	**Chair: Eli Grigorova** **Hall D**
12:20 12:45	Developments in the use of Functionalized Boron Nitride in Composite Membranes for PEM Fuel Cells Applications M-31 Huzaifa Mohammed Adam Harameen , **Ramiz Gültekin Akay** and Shokrullah Hussaini	Matching Electrochemical Properties and Phase Transformations in NASICON-type Electrode Materials for Na-ion batteries S-25 **Maxim Zakharkin**	Influence of atomic configuration on popular descriptors for oxygen evolution reaction on complex transition-metal oxide catalysts S-29 **Dina Mazitova**
12:45 13:05	Nitrogen-doped graphene oxide as innovative catalysts for PEM Fuel Cells M-83 **Adriana Marinoiu** and Elena Carcadea	Investigation of the Mechanisms of Polaron Conduction in Cathode Materials of Na and K-Ion Batteries. S-23 **Olga Kovaleva**	Fabrication of Ordered Mesoporous Nickel Oxide Based Thin Film Electrodes and Their Electrochemical Properties M-64 **Assel Amirzhanova** and Ömer Dağ
13:05 13:25	Bibliometric Analysis of Photocatalytic CO2 Reduction M-77 **Pınar Özdemir** and Ramazan Yıldırım	Key aspects for the development of hard carbon anode materials with advanced performance in sodium-ion batteries S-37 **Zoya Bobyleva**	Development of Z-scheme Heterojunctions for Photocatalytic Hydrogen Production M-146 **Çağla Ünal**, İhsan Emre Yiğiter and Fatih Pişkin
13:25 13:45	Nitrogen-Doped Electrocatalyst from Tangerine Peels-Derived Biochar for Energy Storage and Conversion Applications M-29 **Hilal Doğan** , Tuğba Meşeli, Gamze Genç and Gülşah ELDEN	Investigation of Charged Germagraphene as a Cathode Material for Dual-Carbon Batteries M-60 Burcu Üçok and Taner Akbay	Potential reuse of the Pd-Cu-BTC for reductive sorption of aqueous Hg(II) by thermal desorption technique S-16 **Nurbek Nurlan**
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18th July J2023 (Tuesday)

	Chair: **Hasan Göçmez** Hall C	Chair:**Jasmina Grbović Novaković** Hall B	Chair: **Damla Eroğlu Pala** Hall D
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15:25 15:45	Facile Synthesis of Cross-Linked Carbon Nanofiber Derived from PAN/Thiourea/Aluminum acetate as Supercapacitor Electrode M-133 **Ümran Kurtan** and Serkan Naci KOÇ	Hydrogen storage materials on the basis of Ti–Fe alloys: state-of-the art and perspectives M-100 **Mykhaylo Lototskyy** , Valentin Fokin, Fokina Evelina, Artem Arbuzov and Boris Tarasov	Synergistic effect of Ni/TiO2 heterostructures on performance enhancement of lithium-sulfur batteries S-12 **Nurzhan Baikalov**
15:45 16:05	Production of a ZnS-based Supercapacitor Electrode Material Recovered from the Electric Arc Furnace Dust Waste M-123 **Ozan Aydin** , Burak Birol and Metin Gwnçten	(Bi)Metallic amidoboranes – synthesis, characterisation and perspective for hydrogen storage M-88 **Igor Milanovic** and Nikola Biliškov	Nonosized LiFePO4 manufacturing by ball-milling synthesis for Li-ion batteries S-36 **Batukhan Tatykayev**
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Coffee Break

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17:10 17:35	Charge transport kinetics at a cathode-solid electrolyte interface studied by µ-cavity electrode S-11 **Sung Soo Kim**
17:35 18:00	Improving electrochemical performances of sulfide-based solid battery by understanding and designing interface of cathode/electrolyte S-6 **Lianqi Zhang**
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19th July 2023 (Wednesday)

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10:30 11:00	Transition metal nitrides in ammonia production: Challenges and Possible Solutions M-124 Vanessa C.D. Graça, Francisco J.A. Loureiro, Laura I.V.Holz, Sergey M. Mikhalev and **Duncan Paul Fagg**
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11:30 12:00	Energy Conversion in Solid Oxide Cells: Gaining In-Depth Understanding through Model Experiments M-17 **Alexander Opitz**

	Chair: Mehmet Nurullah Ateş **Hall C**	**Chair: Aliya Mukanova** **Hall B**	**Chair: Müslüm Demir** **Hall D**
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	19th July 2023 (Wednesday)
19th July 2023 (Wednesday) **Poster Session**	**Chairs: Aliya Mukanova** and **Berke Pişkin** **Poster Session** **Main Hall**
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	Atomic structures for ABO3 perovskite S-58 **Zhadyra Zakiyeva**
	Research of hybrid perovskite – low dimensional materials S-56 **Balzhan Satanova**
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	Friction and wear characterization of Si3N4 – SiC nanocomposite ceramic S-39 **Amine Charfi**
	Effect of Ultrasonic Probe Power on the Production of Hexagonal Boron Nitride Nanoplates S-63 Lutfullah Mucahit Dogdu
	Effect of NH4F additive on the electrical properties of nanosized tin dioxide films obtained from lyophilic and lyophobic film-forming systems S-43 **Sayora Ibraimova**
	Friction and wear characterization of Si3N4 – SiC nanocomposite ceramic S-39 **Amine Charfi**
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	Effect of A-site dopant on hydrogen La1-xMxAl1-yMny (M=Na and Sr) perovskite oxides for thermochemical water splitting applications M-112 **Müzeyyen Özdemir** and Berke Piskin
	Electrochemical fabrication and reductive Li-doping of TiO2/ERGO nanocomposite as photoanode for photoelectrochemical water-splitting M-155 **Zeynep Başaran Yılmaz** , Ekin Akyürek and Ümit Demir
	Enhanced visible light photoactivity of Magnesium-doped TiO2/ERGO nanocomposite electrodes for efficient photoelectrochemical water splitting M-156 **Ekin Akyürek,** Ebru Turgıt Him and Ümit Demir
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	Hydrogen Generation by Hydrolysis of Novel Mg-Based Composites M-52 Ihor Zavaliy , Vasyl Berezovets, Andriy Kytsya, Oleksandr Kononiuk and Volodymyr Yartys
	Hydrogen evolution reaction from brass nanostructures M-95 **Tijana Pantić**, Anđela Mitrović Rajić, Sanja Milošević Govedarović,Igor Milanović, Anna M. Brudzisz, Damian Giziński, Wojciech J. Stępniowski, Jasmina Grbović Novaković
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	Development of High Entropy Perovskite Oxides for Thermochemical Water Splitting M-128 Hakan Yüce , **İhsan Emre Yigiter,** Berke Piskin, Fatih Pişkin and Gülhan Çakmak
	Investigation of capacitive and photocatalytic properties of FTO-ERGO/TiO2/Al nanocomposites for energy applications M-157 **Ebru Turgıt Him**, Zeynep Selin Başaran Yılmaz and Ümit Demir
	X 2 FeSi Heusler alloys: A Promising Class of Magnetic Materials S-57 **Merali Nurpeiis**

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	Innovative electrodes for PEM fuel cells based on graphene materials M-89 **Adriana Marinoiu**
	Kinetic behavior of MgH2-transition metal composites: towards hydrogen storage M-98 Zorana Sekulić, Bojana Babić, Milica Prvulović, Igor Milanović, Katarina Tošić, Vanja Asanović, Nikola Novaković, Sanja Milošević Govedarović, **Jasmina Grbović Novaković**
	Protective coatings based on CrN for current collector materials of molten carbonate fuel cells M-86 **Viktoriya Podhurska** ,Yaroslaw Milewski , Olexsander Kuprin[3] and Olena Reshetnyak
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The NLV: A new ultra-fast charging technology for lithium ion batteries

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One of the limiting factors of the electric vehicle (EV) market integration is a long charging time. High energy density batteries are needed to insure a long driving range. However, high energy density batteries do not sustain continuous high current flow to fast charge them because of overheating and possible lithium plating on the graphite anode. High power density batteries on the other hand, can be fast charged but the lack sufficient driving range, which is highly required for EV. Currently, there is a tradeoff between energy and power when the charging method is based on one- or multi-stage constant current (CC).
Here we show that changing the charging method from CC-based to multi-stage constant voltage (MSCV)-based method elevates the issue between high-energy and high-power density batteries. The newly developed method for ultra-fast charging is coined as Nonlinear Volatmmetry (NLV).

In NLV a series of ascending voltage steps are applied while the charging current response, which is not constant, is analyzed. We established a relationship between the applied voltage and the flowing current enabling a transfer from one voltage plateau to the next voltage plateau. NLV enables cutting the charging time recommended by the battery manufacturer by 2x to 5x according to the battery chemistry, state of health and design.

Figure 1 shows a typical voltage and current profiles during charging a battery from 0 to 100% in about 15 min. For such a battery, the standard charging time with CC-based method is 60 minutes. Figure 2 shows the corresponding temperature profile, which did not exceed 42C.

We then successfully applied NLV to several battery packs ranging for 20V to 60V. The 5 to 15 cells in series-based packs behaved like single cells regarding the charging time and temperatures with the only differences lying on the voltage profiles. We also applied NLV to several cells arranged in parallel. A combination of cells in series and in parallel opens the NLV application to larger battery packs for EV.

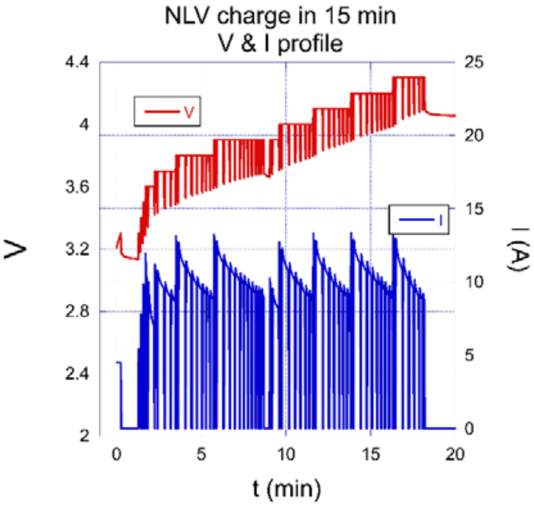

Figure 1: Voltage and current profile during NLV charging in 15 minutes.

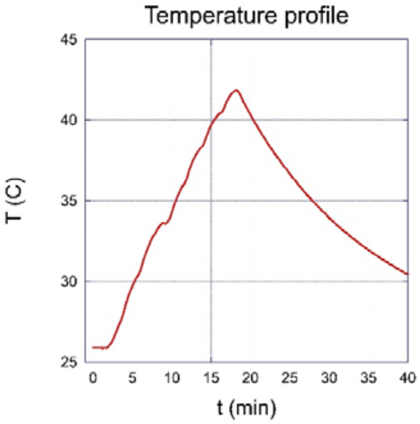

Figure 2: Temperature profile during NLV charging in 15 minutes.

Professor Rachid Yazami is a graduate of the Grenoble Institute of Technology with major in materials science and electrochemistry. He is the inventor of the graphite anode used in current lithium-ion batteries. Yazami has over 40 years long in academic and applied research activity relating to batteries. He is the inventor of 180 patents according the WIPO website. Currently, he is the founding director of KVI Pte Ltd in Singapore which develops battery management methods and systems using artificial intelligence

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Prospects in Battery Energy Storage Over the Next Decade

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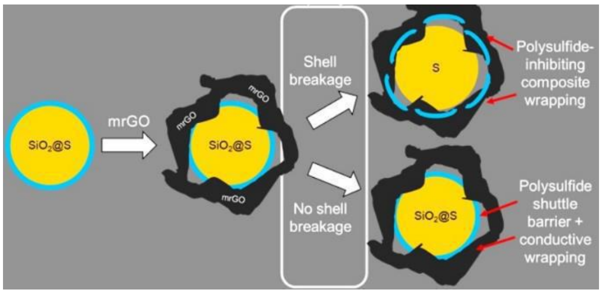
The global electrochemical energy storage market ranging from electric vehicles to physical grid storage demands the development of key enabling technologies for high-energy long-life rechargeable batteries. I will describe the current state of the art and upcoming innovative approaches for the next decade on the design and synthesis of nanostructured materials towards enhanced reversible capacity; superior rate performance and cycling stability; superior gravimetric capacitance; and enhanced energy and power densities.

Silicon (Si) has been proven to be a very promising anode material due to its highest known theoretical capacity value of 3572mAh/g corresponding to the formation of $Li_{15}Si_4$ phase under ambient temperatures. Significant academic and industrial efforts have been made on the synthesis of silicon materials and novel binder systems to mitigate the volume expansion problems. Synthesis of monodisperse Si and C nanocomposite spheres via a facile magnesiothermic reduction with subsequent CVD process has been demonstrated. The monodisperse and high symmetrical nature of the composite spheres allow a homogeneous stress-strain distribution within the structure during charge and discharge cycles. Anode half cells based on MSNSs demonstrate an ultra high reversible capacity of 3207mAh/g along with enhanced cycling stability, improved ICE and rate performance.

Our recent work introduced a scalable industrial mature route to transform polyethylene terephthalate (PET) plastic waste into a superporous activated carbon material for rechargeable LIBs. Carbon-silicon composite anodes were derived by eletrospinning of PET dissolved precursors, pyrolysis under controlled pressure and temperature, and impregnation with silicon nanoparticles (SiNPs) into a superporous connected architecture network. Impregnation with silicon nanoparticles (SiNPs) into a superporous connected architecture network to produce a material with relatively high specific capacity of 201.31 mAh/g at a C/5 rate is demonstrated. Furthermore, half cells based on waste glass Si-C anodes exhibited nearly 1700 mAh/g after 300 cycles at C/2. The theoretical capacity of Li–S cathodes is 1675 mAh/g, and sulfur offers a relatively low-cost battery due to relatively high abundance.

I will describe our work on facile wet synthesis of SiO_2-coated sulfur particles (SCSPs) as potential Li–S battery cathodes. SiO_2 has the inherent ability to surface-adsorb polysulfide species that are soluble in the electrolyte, which deters the loss of electrochemically active sulfur over numerous cycles. Our sulfur cathodes demonstrated superior cycling stability when coupled with mildly reduced graphene oxide (mrGO) as an additive, improving the capacity retention after 50 cycles from 440.8 mAh/g without mrGO to 763.2 mAh/g with mrGO. To further mitigate with the shuttle effect, the sulfur electrodes are coated with TiO_2 thin films, which provides a favorable solid–electrolyte interphase layer owing to the LiPs adsorption properties of TiO_2 layer and the confinment of the LiPs inside the cathode region.

I will describe more recent efforts on solid state batteries in the remainder of my talk. Especially the need for electrical vehicle storage and fast charging requirements necessitate the development of all solid state batteries (ASSLIBs). With the conductivity values reaching above 10^{-2} S cm^{-1} level, solid state electrolytes can compete with the widely commercialized liquid organic electrolytes. Compared with traditional liquid lithium-ion batteries, the manufacturing cost gains an advantage by eliminating the electrolyte injection process; however, the large-scale production of the oxide-based ASSLIBs is critically hindered by its raw material cost and high-temperature (>1000 °C) sintering cost, leading to an estimated overall manufacturing cost of around 180 $ kW/h. Besides, the insufficient mechanical stability of oxides SSE as the thickness diminished below 100 μm resulted in another manufacturing challenge. In general, ASSLIB, composed of lithium metal anode and sulfide SSE, is a cost-effective option for next-generation EV and consumer electronics batteries, especially considering the reduced cell size and safety measurements in practical applications while maintaining or surpassing current LIBs energy density. However, barriers such as interfacial degradation and high total resistance impede ASSLIBs from marching into industrial-scale productions. The overall cell resistance is mainly contributed by ion diffusion in SSEs and electrodes and interfacial resistances. With the guidance toward fast ionic charge transfer and stable interface, mitigation approaches are being adopted, including wetting, polishing, and removing impurity phases are a strategy to decrease the interfacial resistance.



Ozkan received his Ph.D. degree in Materials Science and Engineering at Stanford University. He made pioneering advancements in the fields of Li ion batteries and supercapacitors; nanoelectronics; 2D materials including graphene and dichalcogenides and nanopatterning for beyond CMOS. He is a Member of the National Academy of Inventors, a Fellow of the Materials Research Society, and received a number of awards including the William Johnson International Founders Award, and the TUBITAK Presidential Scientific Achievement Award. Ozkan was elected a Meeting Chair for the Fall 2021 MRS Meeting in Boston, MA

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Connecting solar- and wind electricity to the grid drastically increase interest in aqueous batteries

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Aqueous batteries are low cost because of at least three factors; cheap raw materials, minimal requirements for manufacturing environments, and a limited need for battery management and protection systems. Cheaper material cost because water and the mineral solutes used in traditional aqueous electrolytes, such as H_2SO_4 and KOH, are far cheaper than superdried organic solvents and fluorinated salts, such as $LiPF_6$, used in lithium-ion batteries.

The Edison NiFe battery appeared in beginning of last century, was followed by the NiCd battery when Valdemar Jungner tried to control the parasitic hydrogen evolution reaction in the Edison battery by adding Cd to the Fe-electrode. The Nickel-hydrogen (NiH_2) battery became a preferable choice in space application due to its long cycle life. The NiMH substituted much of the NiCd market with its better capacity. More recently the NiZn is gaining interest with its lower cost of production and high capacity as reflected in a new European battery project LOLABAT, (Long lasting batteries) that aims to bring NiZn back, with funding from the European Union's Horizon 2020 under grant agreement No **963576**. https://www.lolabat.eu/

The NiZn battery was also patented by Edison but never made it into mass production. It has, however, similarities with the NiCd battery but Zn is much more available and environmental beneficial than Cd. The Zn-electrode can also be combined with an air-electrode, further increasing battery capacity and as well as open up for very large sustainable, storage solutions.[1]

This talk will give a background to the chemistries, review recent development and put focus on problems to be solved.

1) Boosting the performance of Zn-air cells by spinel catalysts with bimodal pore structure and gill filament configuration. Hu W.-K., Bai, Y., Yao S., Liu Q., Xu X., Lv T. and Noréus D., *J. Alloy Compd*. **936** (2023) 168185.

Dag Noréus earned his PhD degree in reactor physics in 1982 at the Royal Institute of Technology, Stockholm, Sweden, and completed his postdoc at Daimler-Benz, Metal Hydride Laboratory, Stuttgart, Germany, in 1983. He became a professor in 2000 at the Department of Structural Chemistry, Stockholm University. His research interests include x-ray diffraction, elastic and inelastic neutron scattering, and electrochemistry focusing on rechargeable aqueous battery systems
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Breakthrough in enhancement of hole mobility in strained germanium semiconductor leads to emergence of new class of quantum materials

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Semiconductor materials are the foundation of modern electronic, photonic, photovoltaic, thermoelectricand many other semiconductor devices, which are integral for computers, mobile phones, gadgets, homeappliances, cars and other equipment. More than 99% of all semiconductor devices are made of or on silicon (Si) wafers. Novel group IVsemiconductor epitaxial structures composed of Si, germanium (Ge), carbon or tin on Si wafers provide a natural route for continued improvement of properties of state-of-the-art Si devices with enhanced or emerging unique properties.

Mobility of free carriers in conduction (electrons) or valance (holes) bands, along with a reasonably large energy band gap, is one of the most important quality measures of any semiconductor material, determining its suitability for applications in a large variety of classical electronic, optoelectronic and sensor devices, as well as for novel applications in emerging quantum devices. Higher mobility enables faster operation of a device at lower power consumption and thus leading to reduced Joule heat dissipation, which is essential to minimize for continues circuit scaling as well for increasing the speed of current electronic devices. This is even more important for those devices and electronics to operate at cryogenic temperatures, for example, to control distributed registers of quantum processors.[1] Also, carrier mobility is the critical quality of a semiconductor material for quantum devices, often playing a key role towards new discoveries.[2]

Germanium is a semiconductor material that has been used in the semiconductor industry since the invention of the first transistor. It has some advantages over other semiconductors such as Si and various III-V compounds. In particular, if the mobility of holes in Ge can be enhanced through strain engineering, this could lead to the development of new types of quantum materials with unique properties. Quantum materials are materials that exhibit unique electronic and magnetic properties due to their quantum nature, and they are being studied for a wide range of applications including quantum computing, sensing, and energy storage. Semiconductor heterostructures on Si have a built-in strain that is induced by the mismatch of the crystal lattices of the composed materials. It is an essential parameter used for energy band structure engineering of a material.

Recently, a record-high mobility of holes, reaching of 4.3×10^{6} cm^{2}V^{-1}s^{-1} in an epitaxial strained Ge (s-Ge) semiconductor, grown on a standard Si(001) wafer was reported.[3] This significant increase of the mobility by over four times, compared to the state of the art, allows holes to outperform electrons in theg roup-IV semiconductor materials, for the first time. The demonstrated hole mobility in s-Ge is double that of the best mobility of electrons reported in state-of the art strained Si.[4] A similar situation has not been observed for any other semiconductor material system.

In addition to the record mobility, this material platform reveals a unique combination of properties, which are a very large and tuneable effective g*-factor, a low percolation density and a small effective mass. This long-sought combination of parameters in one material system is important for the research and development of low-temperature electronics with reduced Joule heating, and for quantum electronic circuits based on spin qubits, including devices for Majorana Fermions.[2]

This major breakthrough was achieved due to the development of state-of-the-art epitaxial growth technology culminating in superior monocrystalline quality of the s-Ge material system with a very low density of background impurities and other imperfections. This superior material system with the combination of unique properties will lead to new opportunities for innovative quantum device technologies and applications in quantum as well as in classical electronics, optoelectronics and sensors.

This achievement reduces the gap between the best hole mobility in gallium arsenide (GaAs) heterostructures grown on the same material substrate, which was just recently increased from 2.3×10^{6} cm^{2}V^{-1}s^{-1} to 5.8 cm^{2}V^{-1}s^{-1}.[5,6] Unfortunately, III-V materials are complicated to process, expensive, not widely abundant in the Earth's crust compared to Si and Ge, do not exist in isotopically pure forms, and are not compatible with the state-of-the-art Si technologies for mass production. All other known semiconductors, including III-V, II-VI, perovskites, 2D materials, etc. show substantially lower hole mobility than in the s-Ge and GaAs heterostructures.

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Current status and pillars of direct air capture technologies

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Climate change calls for adaptation of negative emission technologies such as direct air capture (DAC) of carbon dioxide (CO_2) to lower the global warming impacts of greenhouse gases.

DAC can help with hard-to-avoid carbon emissions from distributed sources (transportation, wildfires) and from natural gas processing, the production of cement, iron, steel, ammonia, and urea, biofuel use, and more, helping to offset the nearly 1.9 billion tons of industrial CO2 emissions per year that cannot be feasibly avoided using production technologies.[1]

Recently, elevated global interests to the DAC technologies prompted implementation of new tax credits and new policies worldwide that motivated the existing DAC companies and prompted the startup boom. There are presently 19 DAC plants operating worldwide, capturing more than 0.01 Mt CO_2/year. DAC active plants capturing in average 10,000 tons of CO_2 annually are still in their infancy and are expensive.

DAC technologies still need to improve in three areas: 1) Contactor, 2) Sorbent, and 3) Regeneration to drive down the costs. Technology-based economic development in all three areas are required to achieve <$100/ton of CO_2 which makes DAC economically viable. Current DAC cost is about 2–6 times higher than the desired cost and depends highly on the source of energy used.

The implementation of DAC faces two major technical challenges: (1) energy and (2) materials. Current CO_2 emissions reach nearly 32.6 gigatons/year. With the assumption that only 25% of total CO_2 emissions would be captured, implementing existing liquid and solid sorbent DAC systems would require 10%–20% and 30%–50% of the total global energy supply, respectively. This includes the energy needed to produce sorbent materials and sorbent regeneration. High energy demand could raise the final cost of carbon capture; therefore, inexpensive and low-carbon energy sources are vital. The current goal for DAC is to keep the cost at \$100/tCO_2.[3]

Sorbent material production must also ramp up to meet the demand for DAC scaling. For example, to capture 25% of the total CO_2 emissions per year, sorbents must be produced on the gigaton scale, requiring 20 to 30 times more NaOH, NH_3, and ethanol than is currently produced. Similarly, steel and other construction materials have to scale up, too. The sustainability of DAC will depend on the use of affordable, low-carbon, and low-power capture technologies and stable and selective sorbents with a shortage-free supply chain.

In this presentation, I will talk about the current status of commercial DAC technologies and elucidate the five pillars of technology including capture technologies, their energy demand, final costs, environmental impacts, and political support. I will explain processing steps for liquid and solid carbon capture technologies and indicate their specific energy requirements. DAC capital and operational cost based on plant power energy sources, land and water needs of DAC will be discussed in detail. At 0.01 Mt CO_2/year capture capacity, DAC alone faces a challenge to meet the rates of carbon capture described in the goals of the Paris Agreement with 1.5–2°C of global warming. However, DAC may partially help to offset difficult to avoid annual emissions from concrete (~8%), transportation (~24%), iron-steel industry (~11%), and wildfires (~0.8%). [2]

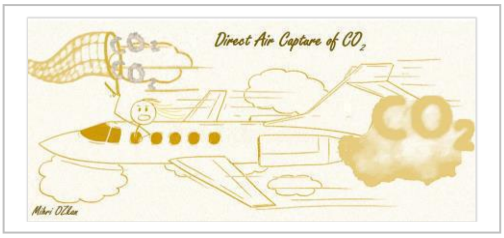

Figure 1. Cartoon expression of DAC.
Prepared by Mihri Ozkan.[1]

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Solid polymer electrolytes for future energy storage devices

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With the global trend of decarbonized energy concerns and decreasing dependence on non-renewable energy sources, next generation energy systems have shifted towards renewable energy sources [1]. In recent years, the global electric power technologies such as electric vehicles (EVs), wearable and portable electronics, smart e-textiles, internet-of-things (IoT) devices, aircraft and aerospace energy are looking for significant developments of current energy storage devices [2]. Current electrochemical energy storage devices such as market leading lithium-ion batteries (LIBs), supercapacitors (SCs) etc. are struggling with serious challenges such as Li-dendrite penetration, safety issues due to internal short circuiting, lower voltage windows, lower energy density and higher self-discharge rate etc. In this context, solid polymer electrolytes, as a one of the significant components for energy storage devices, have been received a huge amount of modern research interest due to their exceptional physical and chemical properties, such as wide electrochemical stability window, leakage free, good flexibility, low flammability, excellent processability, high safety and higher thermal stability [3,4]. Therefore, the design and development of new solid polymer electrolytes can be one of the promising solutions to solve above mentioned issues. The way to design and prepare electrode and electrolyte materials and fabrication of devices are always the vital points to improve the overall performance of future supercapacitors and batteries. Being for the aerospace applications, lightweight power storage supercapacitors are also suitable for powering satellites through decentralized power supplies when they are on the dark side of the raceway and for use on board of e-aircrafts and can be integrated into systems and structures. On these lines, we concentrated our recent studies on the development of lightweight, flat-structured cells with stable solid and/or semi-solid polymer electrolytes incorporating highly conductive and non-flammable electrolytes such as ionic liquids leading to high voltages and longer cycle numbers. In this context, a general overview on the importance of solid polymer electrolytes in terms of energy storage, their working processes, will be demonstrated with examples from our ongoing research and worldwide work. Overall, it is observed that sustainable new solid polymer electrolytes can be an essential component for future energy storage devices while focusing on performance, sustainability, and economy considerations. Accordingly, current challenges and future perspectives for the development of high-performance solid polymer electrolyte will be highlighted.

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Design and Manufacturing of Battery Cells – Aspilsan Perspective

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Ever since Sony released first commercial lithium – ion cells, lithium-ion battery technology still draws attention as a promising energy storage technology regarding to have high energy density, high power density, and long cycle life. The technology then became one of the most researched topics in academia and in the R&D facilities all around the world.

In Europe a research initiative, BATTERY 2030+, has a vision of advancing the sustainable batteries of the future, providing European industry with disruptive technologies and a competitive edge throughout the battery value chain and enabling Europe to reach the goals of a climate-neutral society envisaged in the European Green Deal. The main objectives will be to facilitate and monitor the implementation of the BATTERY 2030+ roadmap, and contribute to European curricula in battery technologies.

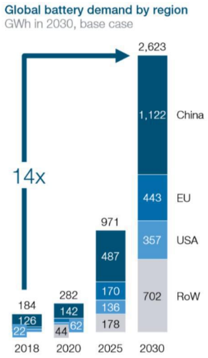

Figure 1. Global battery demand by region [1]

The Turkish Ministry of Industry and Technology has provided support for battery and cell production by offering project-based state incentives to companies such as TOGG, ASPİLSAN Enerji, Pomega and Ford Otosan. Additionally, the Ministry's "Leap (Hamle)" program, within the framework of the Mobility Roadmap, has granted incentives to 31 firms in various fields, including autonomous driving, electronic vision, vehicle structures, and battery management systems.

The opportunity of domestic battery manufacturing as this market grows, the challenge is that Türkiye is not a large producer of minerals such as lithium, manganese, cobalt, or graphite, etc. These are important components of today’s lithium-ion batteries. However, Türkiye has a potential to become a significant player in battery production within its region. To achieve this, Türkiye needs to manage the entire value chain, ranging from mining and recycling to cell design and turnkey factory establishment, as well as machine manufacturing and testing equipment. The country's robust industrial infrastructure, skilled workforce, and technical expertise make it capable of taking ownership of the entire battery production process. Additionally, Türkiye's geographical location offers important advantages for collaboration and serving as a vital hub between raw material suppliers and manufacturers.

To achieve these milestones, first significant attempt in the country is performed by ASPİLSAN Enerji by starting the manufacturing with 220 MWh/year of the energy capability. This mass-production started by using an accredited 18650 type cell design in 2022. The design is owned by ASPİLSAN Enerji and this step has brought a great deal of know-how about the design of cells and the key components of batteries such as active materials, solvents, binders, electrolytes, and foils. Battery cell design and manufacturing often require customization to meet specific industry or application requirements. Companies like ASPİLSAN Enerji may focus on developing tailored solutions that address the unique needs of their customers, whether it's related to energy density, power output, size, weight, or safety considerations.

For Türkiye to become a regional battery hub, it must engage in activities spanning the entire value chain, from mining and production to recycling, testing, and certification. Battery production thrives on economies of scale, and if Türkiye's production capacity reaches the Terawatt scale, it can create a significant market for manufacturers involved in the entire process. Although the current investments in Türkiye are still at the Gigawatt scale, there are substantial opportunities for entrepreneurs in European and American battery investments. Consequently, Turkish initiatives addressing the outlined needs in battery production and testing processes can capitalize on significant opportunities in the Western market, particularly due to the embargoes imposed on China.

Figure 2. ASPİLSAN Enerji cell production facility.

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Batteries for Grid Energy Storage

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The future of renewable energy, primarily solar and wind, depends on the development of energy storage technologies and their safe, longer lasting and cheaper applications. Since the power produced from solar and wind has grown quickly over the past decade, further integration of those in the grid is becoming increasingly difficult based on their unpredictable and intermittent nature. This challenge for the grid brings the popularity of energy storage systems, offering absorbing electricity from the grid when it is plentiful and release when needed.

Energy storage systems (ESS) increase the renewable portion of electricity delivered to the customers and thus significantly reduce emissions associated with fossil fuels. Those systems also help overall grid performance by making grid's conventional power plant management easier and providing more options in case of emergency. Other than renewable energy integration, grid services including energy arbitrage, peak shaving, spinning reserves and frequency regulation are mostly used and dominant services that ESS easily handle. In spite of the fact that the certain types of ESS such as redox flow, electrochemical batteries and compressed air provide those services, lithium-ion batteries appears to be the most suitable technology with its cumulative advantages.

ESS installation is projected to grow 15x installed capacity in 2021 to reach 1194 GWh by 2031 [1]. Li-ion-based especially Lithiumiron phosphote based ESS is likely to dominate for the next decade due to price competitiveness, while emerging non-Li-ion technologies progress towards demonstrations/commercialization for utility markets.

Figure 1. The cumulative energy storagemarket by segments (Gwh **)**

ESS system grid services' cumulative effectiveness with its safety, quality and reliability from single Lithiumiron phosphote cell to huge high voltage battery clusters is the main topic for R&D activities in Pomega Energy Storage Technologies Inc.

Pomega Energy Storage Technologies Inc., one of the subsidiaries of Kontrolmatik Technologies, is the first and only private company for the Lithium Iron Phosphate Battery Cell Giga factory in Türkiye and Europe. The plant, which will be commissioned in the third quarter of 2023, will reach a total annual production capacity of 2.25 GWh when all phases are completed by 2024.

Pomega Energy Storage Technologies Inc. responds to the increasing demand of the industry by producing Lithium Iron Phosphate battery cells, battery packs and energy storage systems. These products are the best solutions for power plants, national grids, factories, household applications, and areas requiring high power.

The applications for Pomega Batteries are cabin type, container type, and household energy storage systems, electric car charger mobile support systems, hybrid renewable storage containers, and stationary energy storage products that provide energy storage solutions to network operators, electricity market components, industrial customers, and operators of electric charging stations.

Battery packs including BMS are offered for heavy electric vehicles such as construction machinery, trucks, and buses and light commercial vehicles such as forklifts, golf carts, and man lift.

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Uğur Kazancıoğlu completed his undergraduate and graduate education at METU Electrical and Electronics Engineering Department. By starting his career in Aselsan Inc. in 2004, he continued R&D activities on control and power electronics as a design engineer, a team leader and a power&control systems department manager up to 2018. He worked as R&D Manager for Basari Energy Inc. and Megart Technology Inc. which are developing technologies for renewable energy and defense sector between 2018 and 2022. He contributes to R&D activities on lithium-ion battery systems from single cell to complete ESS and storage power converter systems as R&D Manager in Pomega Energy Storage Technologies Inc. since 2022.

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Kazakhstan State Program on Advanced Materials for Energy Storage

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Lithium-ion batteries leading the path as a power source and storage device for various applications from portable electronics and electric cars to large scale energy storage systems. This is due to their superior performance in terms of high energy density, stability, reliability, rapid operation and many other advantages compared with other types of batteries and energy storage means. However, emerging applications especially in consumer electronics and electric transport demand even better performance batteries, which can be made in a variety of shapes and sizes, conform with flexible and wearable applications, capable to work in extreme conditions, and all these combined with and exceptional high safety and lower cost.

These demands encouraged the development of a research program to address the above challenges for batteries for flexible applications, low temperature operations, thin film and microbatteries, and safe large scale energy storage from renewable sources. This Program considers not only technological developments but also training of researchers and involves a large number of students. The Program structure and progress will be discussed at the conference.

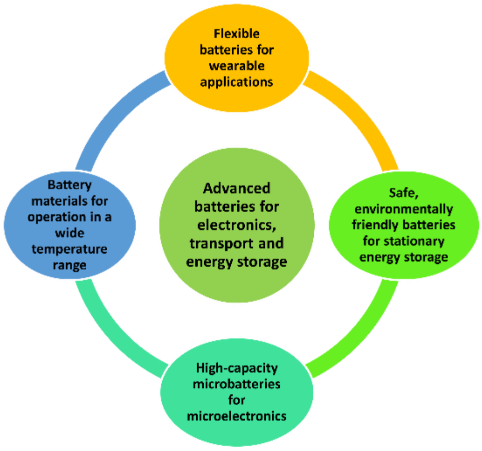

Figure 1.Research directions of Program

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Türkiye Hydrogen Technologies Strategy and Roadmap

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Ministry of Energy and Natural Resources have declared that hydrogen as one of the priority areas for building a carbon-neutral economy model by using hydrogen. By achieving this vision, "Türkiye Hydrogen Technologies Strategy and Roadmap" was developed by TENMAK and announced by the Minister on January 2023. It has been emphasized that the green hydrogen will be an important element for the country's net zero emission targets. It was aimed to establish a nationally guided research, technology development support and application program for the domestic development of hydrogen technologies and to determine a strategic action plan beforehand. Within the scope of the report, 20 needs are determined and 31 solutions are offered in terms of production and usage, storage and distribution, industry usage, non-technological needs. The targets of the Türkiye for the hydrogen production are determined as follows:

1. To reduce the cost of green hydrogen production below 2.4 USD/kgH_2 by 2035 and below 1.2 USD/kgH_2 by 2053,
2. To ensure that the installed power capacity of the electrolyzer reaches 2 GW in 2030, 5 GW in 2035 and 70 GW in 2053.

The vision of the report is to play a leading role in the world in the production and use of green hydrogen by developing the most advanced domestic and national technologies. Some policies in the report are determined as follows:

1. By reviewing the current legislation, to make it suitable for "hydrogen production, transportation storage and use.
2. To encourage R&D and P&D for the development and production of domestic and national technologies (electrolyzer, fuel cell etc.).
3. To collaborate internationally on issues related to industry, technology, standards, certification, and development, supply chain and trade opportunities.
4. To export surplus green hydrogen or ammonia to the world and especially to the European Market with our domestic technologies.
5. To use domestic resources especially boron mine in hydrogen storage.

In order to support decarbonization, TENMAK also developed Technology and Product Development Projects Support Program (TUGEP). Hydrogen Technologies and The Fuel Cell Call was opened in 2022 with prioritising the need of our country in the hydrogen technologies field. The three main topics listed below were primarily targeted in the hydrogen technologies call;

1. Clean hydrogen production technologies (with a production capacity of at least 100 kg per day)
2. Storage and liquefaction technologies (high pressure storage tanks, tanks to be produced with new generation materials, sodium boro hydride storage, metal hydride-based absorbent storage, new generation chemical storage systems)
3. Fuel cell technologies (a modular package with a power output of at least 10 kW depending on the application area)

As part of the Roadmap, the R&D and innovation priorities have been elaborated and are summarized by the following areas:

1. H_2 production: development of electrolyser and mass production of hydrogen (boron technologies) in integrated facilities covering safety standards. R&D activities will be carried out for the production of hydrogen and synthetic gas from lignite and organic wastes. In order to increase the production of green hydrogen, it is planned to increase the production and share of renewable energy.
2. H_2 storage and distribution: production of storage facilities such as pressurized tanks for land vehicles, metal hybrids, and cryogenic tanks in the aviation, space and defence industries. Production of H_2 storage systems for stationary and mobile marine and aerospace applications. It is aimed to use domestic resources, especially boron, in hydrogen storage.
3. H_2 use:

3.1. Mobility applications: hydrogen refuelling stations will be installed and expanded in Türkiye to meet the fuel needs. Some of these studies are:

-Storage analysis for pressurized and liquid hydrogen transport vehicle;

-Demonstration studies for hydrogen transport at sea;

-20 kW, 100 kW and 100-300 kW Fuel Cell (FC) land vehicle applications; 20 kW and 200-300 kW FC sea vehicle applications; 10 kW and 100-300 kW FC rail vehicle applications; 5 kW, 20 kW, 50-100 kW and 100-200 kW FC UAV and aircraft applications; 5-50 kW and 50-100 kW fuel cell airport application

3.2. Heat and power: the goals are to achieve 1-20% and 20-100% of a hydrogen natural gas turbine, boiler, etc technology and to blend a quantity of 5-20% and 20-100% of hydrogen in the natural gas grid for domestic and industrial use.

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Materials for Fuel Cells and Electrolysis Technologies: Challenges and Perspectives

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Hydrogen technologies have been at the center of discussions about the future of energy in recent years. Hydrogen is potentially an ideal energy carrier, fuel and a feedstock for various industries. However, several key challenges must be overcome for hydrogen to be used extensively in a sustainable future energy. Electrolysis, the electrolytic decomposition of water to produce hydrogen and oxygen, is very promising for green hydrogen production, yet several challenges need to be overcome. Green hydrogen can be utilized as the fuel for electricity generation by means of fuel cells. In recent years, these technologies have been rapidly evolving to improve the performance, efficiency and durability of electrolysis and fuel cell systems. Polymer electrolyte membrane fuel cells (PEMFC) are attractive energy conversion systems for stationary, and transport applications due to their distinguishing features including high power density, low temperature operation and a compact system. Despite the enormous progress in PEMFC technology there are still core challenges for commercialization including performance, durability, and cost. Similarly, although polymer electrolyte membrane water electrolyzers (PEMWE) are one of the most promising technologies for green hydrogen production, there are certain issues regarding performance and durability of these systems.

In our research group, we have been studying not only synthesis, production and modification of materials /components but also evaluation these materials/components in-situ in these systems for their performance and durability. We have been developing alternative polymer electrolytes, membranes, catalysts, and electrodes to enhance the efficiency and performance of electrolysis and fuel cell systems.

Polymer membrane, which serves as both the electrolyte and separator, is one of the most critical components for both PEMFC and PEMWE. Nafion® membranes have been extensively employed commercial membranes for these systems owing to their good chemical and mechanical stability as well as excellent ionic conductivity at fully humidified conditions. However, due to their high cost and inadequate conductivity at lower humidity levels, new strategies such as replacement of them with alternative cost-effective membranes have been investigated previously. In this regard, we have been developing a new generation of membranes with improved performance and significantly higher durability while using sustainable and affordable materials. Radiation grafted membranes are promising candidates since the method employs inexpensive materials, readily controlled and membranes in the film form can be fabricated without solution casting [1,2]. Electrospinning is another attractive fabrication technique we have employed for nanofiber composite/hybrid membranes. In this respect, hybrid membrane fabrication with organic/inorganic constituents via electrospinning technique is considerably attractive due to long-range organization of hydrophilic and hydrophobic parts in the nano scale. Herein, we summarize our work on dual fiber electrospun membranes, and radiation grafted membranes. Regarding catalysts and electrodes for both fuel cells and electrolyzers, there are still significant challenges we have focused on. Especially, Pt and IrO_2 nanoparticles used as catalyst to enhance reaction kinetics, yet they have high cost, performance and durability problems and low abundance as well. We have been developing various catalysts based on Pt group metals (PGM) and non-PGM highly dispersed, uniformly decorated 2-3 nm, exhibiting high catalytic activity by means of impregnation-reduction, microwave-assisted deposition, photocatalytic deposition, and surfactant assisted deposition methods [3,4].

In this talk, challenges of both fuel cells and electrolyzers and summary of our work on components of these systems will be presented. Various examples of projects we have been involved including Graphene Flagship, the first hydrogen valley of Turkey, HYSouth Marmara, and several other will be depicted.

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RESEARCH METHODS & CHARACTERIZATION

Energy Conversion in Solid Oxide Cells: Gaining In-Depth Understanding through Model Experiments

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Solid oxide cells comprise a large class of electrochemical systems with multiple applications in energy conversion (solid oxide fuel and electrolysis cells), heterogeneous catalysis, gas analysis (lambda sensors), and others. The research questions associated with these cells and their materials range from the optimization of commercialized systems to the basic scientific understanding of electrochemical elementary processes. A sound knowledge of the relevant elementary parameters and current pathways is thereby of great importance both for the application case and for purely academic understanding. Identifying these pathways and disentangling elementary parameters such as ionic and electronic conductivities, reaction resistances, interfacial and chemical capacitances is thus the aim of many research works in this field of science.
Well-defined model systems are a powerful tool to achieve this goal, as they offer the opportunity to exactly knowing the geometry of the studied electrode and to modify it in a controlled manner. This is the basis for drawing sound conclusions about current pathways and relevant elementary parameters. Moreover, this type of samples is an ideal platform for analytical measurements, as their electrochemically active interfaces are easily accessible by surface sensitive techniques. In this contribution, a couple of examples are presented, where model samples based on thin films are employed to extract elementary properties of functional materials used in solid oxide electrochemical devices:
i) The formation and electrochemical switching behaviour of exsolution catalysts was studied by a combination of electrochemical techniques and *in-situ* surface analytical measurements. These experiments allowed extensive conclusions to be drawn about both the switching mechanism and the reaction mechanism of H_2 oxidation/H_2O splitting on metal-decorated perovskite electrodes.

ii) To study the effect of exsolutions on CO_2 electrolysis, *in-situ* near ambient pressure XPS was performed on exsolution decorated perovskite-type electrodes. In this case the polarization induced formation of different carbon species – a carbonate and graphitic carbon – was observed, with the carbonate being regarded as an active intermediate in the CO_2 reduction mechanism.

iii) Finally, it will be shown how the mechanistic understanding obtained on model-type thin film systems can be used to significantly improve the performance of real 3D porous Ni/$Ce_{0.9}Gd_{0.1}O_{1.95-\delta}$ (GDC) electrodes in a knowledge-driven manner. By fitting the measured electrode impedance to the correct analytic transmission line circuit, separation and quantification of the individual contributions to the electrode polarisation resistance is possible, and comparison with model studies yields very good quantitative agreement. Moreover, we can demonstrate that fully oxidic GDC electrode functional layers can even outperform state-of-the-art Ni/GDC electrodes in H_2/H_2O atmosphere and exhibit also excellent kinetics in CO/CO_2.

Alexander K. Opitz is the head of the research group Electrochemical Energy Conversion at TU Wien(Vienna, Austria). There he also received his PhD in 2011. He was a visiting scientist at MIT in 2017 and returned to a tenure track position at TU Wien, where he is now an Assistant Professor in the research division of Technical Electrochemistry. He is doing research in the fields of Solid State Ionics (electrode kinetics, current pathways, and electrochemically active zones of solid state electrochemical systems), heterogeneous catalysis (in-situ spectroscopic and analytic studies on the surface chemistry and catalytic activity of electrodes), and materials chemistry (synthesis and characterization of novel, alternative materials for solid oxide cells).

Impedance and noise as non-invasive methods for lithium metal anodes

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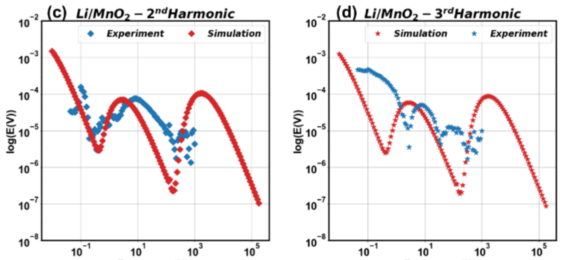
Analyzing battery performance and behavior is critical for not only designing better batteries but also in order to follow the life of electrically powered devices. With the increasing deployment of electric vehicles, being able to evaluate the real-time properties of batteries enables constant monitoring and informed decision-making regarding replacement, fast charge and other critical issues.

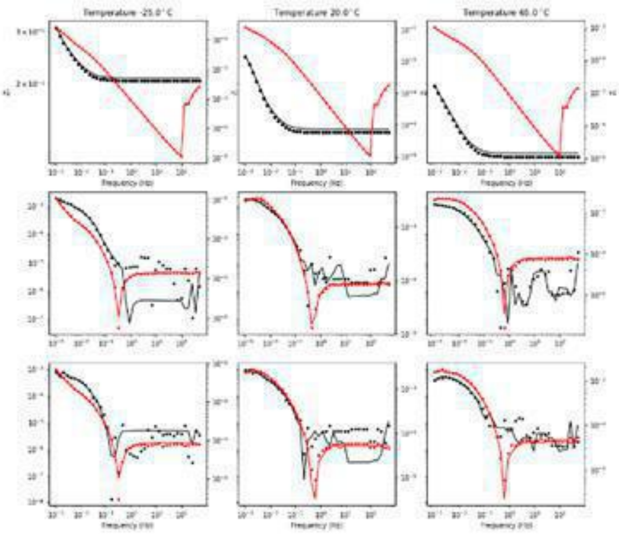
Electrochemical Impedance Spectroscopy (EIS) is a well-known analysis method that is non-invasive. Varying the frequency of the AC excitation applied to the battery under test, different interfaces are excited or by-passed. This in-turn yields electrical signatures of the various buried interfaces without physically disassembling them. Though enormously powerful, EIS is very prone to misanalysing as the equivalent circuit approach that is very commonly used does not result in unique circuits or parameters. This makes the analysis very subjective and prone to questioning. If/when properly analyzed, parameters regarding individual components/interfaces are independently obtained from a complete cell [1].

Electrochemical Noise is an analysis method that is not only non-invasive, but also non-perturbing. In this method, there is no excitation, no signals applied to the device under test. Conventionally, electrochemical noise is employed in corrosion measurements that involve stochastic modes of noise; namely, crevice and pitting. In this method, the signal is measured and analyzed for stochastic events that are not explained by simple instrumental noise or sample related drift. Applying this to batteries is not trivial due to the large magnitude drifts and small intrinsic noise [2]. However, we have successfully employed voltage noise as a predictor of uneven discharge of metallic lithium anodes in non-rechargeable Li\MnO$_2$ batteries.

In this talk, I will be presenting our recent work on EIS and Noise on battery analyses. On the EIS front, I will be introducing extensions of EIS measurements regarding temperature dependence and higher harmonics. The information that is brought in by the extra measurements of higher harmonics and the data from different temperatures allow us to be able to identify the frequencies that various interfaces correspond to and make more detailed analyses. I will present how we are making use of the harmonics and the temperature dependence in order to extract more information.



(a)



(b)

Figure 1. (a) Figures illustrating the calculated and the measured harmonics for batteries based on the initial transient.(b) Fitting the temperature dependence of first, second and third harmonics.

On the noise front, I will be presenting our earlier work showing how and why uneven discharge in lithium metal anodes increase the voltage noise. Further, I will be presenting recent studies that critically evaluates the way noise data is typically analyzed. We will show that simple mathematical manipulation of data can generate visually pleasing figures, but are of little use since subjectively manipulatable parameters end up dictating the final result. I will be emphasizing the use of proper experimental design in evaluating the noise data in order to obtain proper results.

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Integrating Electrochemical Impedance Spectroscopy and Current Interruption Tests for State of Health Detection and Performance Prediction of Lithium-Ion Batteries

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Lithium ion batteries have been a special interest of recent because of its wide use, especially in electric vehicles. Though it has many advantages for its popularity, state of health (SOH) is a big concern for its lifetime and overall perfomance. To elaborate, in the case of electric vehicles, a declining SOH can lead up to declined driving range and power capacity. Further, safety concerns hamper the wide utilization of electric vehicles. Hence, SOH estimation is a crucial part of the maintenance of a battery.

Electrochemical Impedance Spectroscopy (EIS) is a frequently used technique to study several parameters related to batteries. It has been a preferable method as it is non-invasive and applicable in-situ and in real-time. It can also give information about the solution resistance, ion transport and solid electrolyte interface of the battery through gathered spectrum's equivalent circuit fit independently from each other. However, this fit can be made with different elements that give the same mathematical result, which arises from complex reactions that occur in the battery. Thus, different impedance analysis techniques should be utilized for the best interpretations of the results.

To reduce the ambiguity aforementioned, distribution of relaxation times (DRT) can be employed. DRT helps the construction of equivalent circuit fit by turning impedance data gathered in frequency domain into time constant domain. This way, the overlapping peaks are able to be broken down into its constituent peaks, resulting in distinguished elements in the circuit and clearer understanding of the processes occur in the batteries [1].

Moreover, Intermittent Current Interruption can also be used during the cycling of batteries at different states of charge (SOC). This is done by chronopotentiometry followed by lack of applied current. The decay of cell potential that is observed at i=0 and t=0 can be related to the internal resistance and diffusion resistance coefficient of the battery without disturbance [2].

For the standardization and commercialization of the implemetation of the techniques explained, firstly the parameters that will be derived from the techniques should be determined. Following, the conditions that reveal the parameters should be used only to reduce the time for the examinations. Moreover, inspections should not be done for every charge-discharge cycle to make the process more practical, but the number of cycles it will take to observe significant changes should be determined to decrease the number of inspections that must be done. [3]

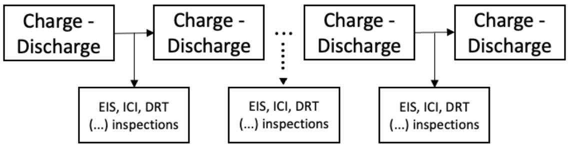

Figure SEQ Figure * ARABIC 1. Flowchart of Electrochemical Measurements.

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R. Ezgi Sevgen is currently in Department of Chemistry Masters Program of Ihsan Dogramaci Bilkent University. She graduated from METU, Department of Chemical Chemistry in 2022. Her interest of research topics can be listed as spectroelectrochemistry of Tungsten Trioxide, Impedance and Current Interruption of Lithium Ion Batteries.

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Li migration and charge transfer through Li/$Li_7La_3Zr_2O_{12}$ interfaces under constant-charge conditions

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Lithium-ion batteries with solid-state electrolyte have a number of superior properties over batteries with liquid electrolyte. Among the advantages of solid-state electrolytes are a wide electrochemical window and better thermal stability. Solid-state electrolytes are potentially compatible with metallic lithium, allowing to increase energy density significantly [1]. If in batteries with a liquid electrolyte, the contact between the electrodes and the electrolyte is excellent due to the filling of all voids with liquid electrolyte, in solid-state batteries, it is difficult to ensure a tight contact between the two solid phases.

At the moment, there are methods to manufacture Li/LLZO interfaces with low resistance, which show small capacity retention over 10–100 cycles. However, all these methods involve modification of LLZO and introduction of an additional phase at the phase boundary [2]. Meanwhile, it is not completely clear why the capacities of batteries with unmodified LLZO electrolyte decline fast, and how the interfaces evolve with cycling. Modeling of interfaces between lithium metal and LLZO with the consecutive study of structure's transformation during cycling can fill this gap.

Electrochemical experiments together with diffraction and microscopy studies provide data on the electrical conductivity of interfaces and, perhaps, regions where conductivity deteriorates. In addition, using the maximum entropy method [3], it is possible to find migration pathways of Li-ions. Yet, such experiments require extensive time and financial expenses, without providing information on the magnitude of migration barriers. In order to investigate and qualitatively characterize the Li-ion migration at the atomic scale with reasonable time and financial expenses, computational modeling is required. At the same time, we study this process on idealized structures with their intrinsic properties, avoiding imperfections that are always present in a real experiment.

In this study, we investigate the migration of Li-ions at the interfaces between $Li_7La_3Zr_2O_{12}$ (LLZO) and lithium metal using density functional theory calculations. We have considered all terminations for the tetragonal phase of LLZO with space group 230. The results of surface energies are consistent with other computational works [4]. Next, we used surfaces with the lowest surface energies to construct interfaces with lithium metal (Li/LLZO). Having selected interfaces with the lowest interface energy and adhesion energy, we investigated migration pathways and barriers in these structures under the constant-charge conditions, as shown in Figure 1. In addition, we studied the influence of uncompensated electric charge at the surface on the shape of the transfer energy profile.

Our results show that charge transfer barriers are moderately larger compared with migration barriers in bulk LLZO. The difference is of the order of 0.2 eV, showing the origin of interfacial resistance observed in the experimental studies [1]. Also, we demonstrate that Li vacancy formation is favored at the interface region, pointing out a possible reason for voids' formation and interface structure degradation.

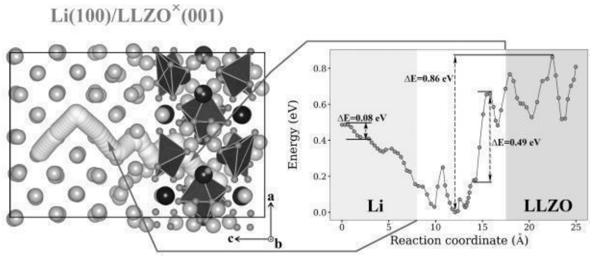

Figure 1. Pathway and energetics of Li-ion migration at Li/LLZO interface under the constant-charge conditions.

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A Novel Approach Enabling Atomic Scale Characterization for Li-on Battery Components probed by Positron Annihilation Lifetime Spectroscopy (PALS)

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Positron annihilation lifetime spectroscopy (PALS), displayed in Figure 1, is a well-established and very sensitive nondestructive spectroscopy technique that allows studying nanodefects in materials such as free volume and its fraction. The PALS spectra were fitted into 3 or 4 parameters, including τ_3 with I_3 and τ_4 with I_4, associated with the pick-off annihilation of ortho-positronium (o-Ps within the crystalline and amorphous regions of the polymers).

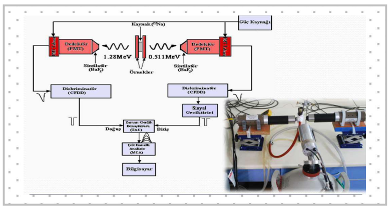

Figure 1. Positron Annihilation Lifetime Spectroscopy

Polymers and their blends have been widely applied in various industries, including energy storage devices. Lithium-ion batteries play a significant role in which electrolytes are critical for transporting positive lithium ions between electrodes. Liquid electrolytes that are currently in use are often flammable, volatile, toxic, and more prone to short circuit and leakage, leading to environmental and safety concerns. To overcome these disadvantages, solid polymer electrolytes (SPEs) have emerged as alternative systems. While SPEs provide decent mechanical stability, deformability and biocompatibility, their low ionic conductivity at room temperature compared to liquid electrolytes remains a major challenge for their commercial use.

Linear poly(ethylene oxide) (PEO) has gained significant attention as an SPE due to its excellent characteristics, including fast segmental dynamics and the ability to dissolve different lithium salts. At room temperature, however, PEO is a semicrystalline polymer with an ionic conductivity ranging between $10^{-6} - 10^{-8}$ S/cm, in which crystalline regions impede ion transport. The ionic conductivity increases up to 10^{-3} S/cm above its melting temperature (T_m = 60°C), yet with a severe reduction in mechanical strength, which limits its application in a solid-state battery. To overcome these drawbacks, one method is to use PEO with another polymer that can provide mechanical rigidity and eliminate crystallinity. In this sense, the high glass transition temperature (T_g) polymer poly(methyl methacrylate) (PMMA) is commonly used. Incorporation of PMMA into PEO significantly increased the mechanical properties, such as the storage modulus, making the liquid-like behavior of PEO more solid-like. Additionally, the effect of free volume on ionic conductivity was investigated by various studies in PEO-based SPEs. The increase in free volume in the polymer matrix resulted in assisted ion migration, enhancing the ionic conductivity in these SPEs. Here, we take advantage of the enhanced free volume due to the increased number of free end groups in nonlinear PEOs and suppressed crystallization arising from branching as well as PMMA addition to facilitate the transportation of Li+ ions in PEO/PMMA-based copolymer electrolytes. Therefore, to relate the free volume of branched PEOs with the ionic conductivity of PEO-grafted PMMA copolymers with varying molecular weights (PEO (1.5 kDa & 20 kDa)) for the temperature range from 30 to 90℃, we employed PALS.

Furthermore, the obtained results from PALS and EIS are displayed in Figure 2 for the free volume estimations as a function of temperature for PEO with increasing branching. In addition, it is evident that there were two different clear trends for the free volume above and below a certain temperature, which turns out to be the melting temperature for PEOs, and this temperature agrees well with the estimations from the differential scanning calorimetry experiments. This changing trend could be well related to the melting crystals and higher branched arms in the PEO matrix, producing significant additional free volume. It is also evident that the enhanced free volume probed by PALS resulted in an increase in ionic conductivity in branched PEO/PMMA systems when compared to the blend PEO/PMMA electrolytes. Eventually, the PALS is planned to be used for structural changes observed in electrodes due to possible reasons such as doping, aging, and cycling.

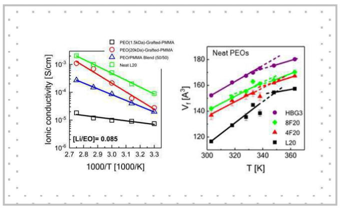

Figure 2. Temperature-dependent ionic conductivity measurements with free volume measurements probed by PALS.

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I specialized in lithium-ion batteries, solid polymer electrolytes (SPEs) polymer physics, rheology, morphology, polymer blends and additives within depth understanding of structure-property relationships of polymers as new functional and smart materials for polymer electrolytes. Currently working as a Cell development R&D engineer at SIRO, focusing on developing novel lithium-ion batteries.

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Computational study of Li segregation and diffusion at grain boundaries in Cu: implications for Li-ion current collectors

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Adoption of Li-ion batteries for stationary energy storage requires to prolong their operational lifetimes to several decades calling to inhibit all degradation mechanisms. It is widely accepted that copper current collector used on the anode side of a commercial Li-ion battery is stable in contact with metallic lithium or LiC$_6$. However, looking at Li-Cu phase diagram one can discover that up to 18-23 at. % of Li dissolves in copper at room T [1]. The thermodynamically favourable formation of Cu-Li alloy upon electrochemical cycling of a Li-ion battery should be accompanied by gradual loss of lithium, increase of the current collector electrical resistivity, and potential decohesion of anode material due to the volumetric expansion of a current collector. Even though such processes are slow, they can limit the lifetime of Li-ion batteries intended to operate during 10-20 years, such as used in electric cars and grid storage.

Indeed, Li penetration into copper foil of a cycled cell was detected by Nagpure et al. using neutron profiling in depth (NPD) method [2]. The penetration depth exceeded 0.8 μm constituting a non-negligible part (~8 %) of a typical current collector foil. The irreversible Li uptake shows that Li is indeed dissolved in copper, while the speed of this process is governed by Li diffusion. The lithium depth profiles by time-of-flight secondary-ion mass spectrometry study shows that Li diffusivity in a single crystal Cu at room T is 1.3 x 10^{-20} cm^2/s, while in a polycrystalline Cu it is increased by three orders up to 1.4 x 10^{-17} cm^2/s due to the enhanced grain boundary diffusion [3].

Interestingly, the nature of Li diffusion in Cu remains poorly understood even in the case of a single crystal. The origin of much faster Li diffusion at Cu grain boundaries (GB) also remains obscure. No information is available about Li segregation at GBs and its impact on vacancy formation and migration energies.

In this study we address the phenomena of Li grain boundary segregation and diffusion in copper by performing density functional theory calculations and explain the origin of favourable Li segregation and decrease of migration barriers using electronic structure analysis. We consider the thoroughly studied $\Sigma5(310)[001]$ symmetric tilt GB (Figure 1) and two experimentally observed twin boundaries: $\Sigma3$ (112)[110] and $\Sigma9$ (221)[110] tilt grain boundaries and generalize results to a wide range of special grain boundaries.

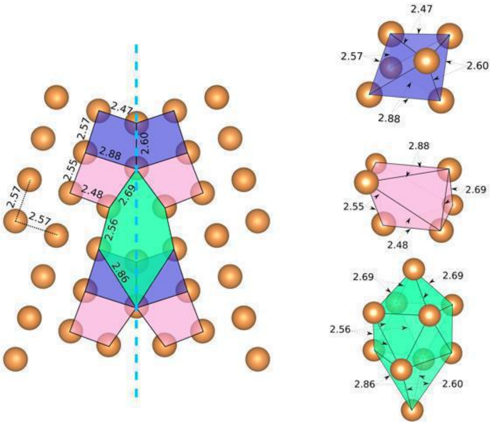

Figure 1. The structure of $\Sigma5(310)[001]$ grain boundary and considered substitutional and interstitial positions for Li segregation and migration.

Overall, we show that grain boundaries promote Li penetration inside the copper thin films due to Li segregation and accelerated GB diffusion which can be a reason for slow Cu electrodes degradation in Li-ion batteries.

Acknowledgements

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Artificial-intelligence assisted search for best energy-conversion materials

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Important properties of energy materials, such as activity and selectivity of a catalyst or a thermoelectric's figure of merit, are in general difficult to predict, in particular from first principles. The problem lies in the extreme complexity of the relation between the atomic composition of a material and its functional properties at realistic temperatures and pressures. We demonstrate how to bridge this complexity with artificial intelligence (AI) on several examples.

Single-atom metal alloy catalysts (SAACs) have recently become a very active new frontier in catalysis research. The simultaneous optimization of both facile dissociation of reactants and a balanced strength of intermediates' binding make them highly efficient and selective for many industrially important reactions. However, discovery of new SAACs is hindered by the lack of fast yet reliable prediction of the catalytic properties of the sheer number of candidate materials. We address this problem by applying a compressed-sensing approach SISSO parameterized with density-functional inputs. Besides consistently predicting high efficiency of the experimentally studied SAACs, we identify more than two hundred yet unreported candidates (Figure 1) [1].

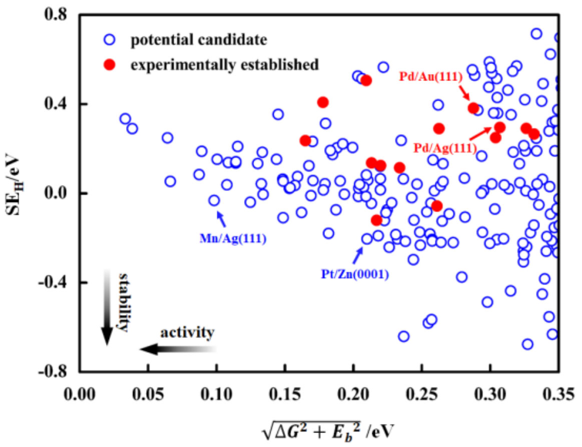

Figure 1. Stability vs. activity map for flat SAACs surfaces at T=298 K and p=1 atm.

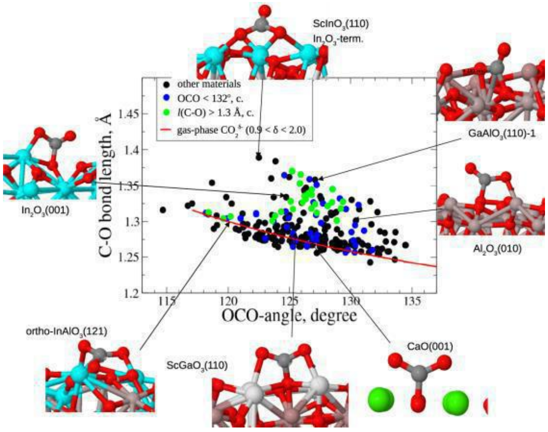

Figure 2. The OCO-angle in charged gas-phase CO2 is shown with the red line, and adsorbed CO2 structures are shown with the dots. The colored dots show the subgroups of best catalysts for two different mechanisms of CO2 activation.

Some of these candidates are predicted to exhibit even higher stability and efficiency than the reported ones. Our study demonstrates the importance of finding descriptors directly from data, as well as provides a recipe for selecting best candidate materials from hundreds of thousands of transition-metal SAACs for various applications.

Employing SISSO in an active-learning framework, we have also predicted and experimentally confirmed stable medium-temperature polycrystalline p-type thermoelectric (TE) materials with a very high figure of merit (~2). This breakthrough became possible due to the AI-assisted exploration of the vast materials space of a known class of TE materials, which allowed us to find materials with an optimal balance between conflicting parameters.

Moreover, using subgroup discovery, an AI approach that discovers statistically exceptional subgroups in a dataset, we develop a strategy for identification of most important parameters of a catalytic material and competing mechanisms of a catalytic reaction. The approach is used to develop physical understanding of hydrogen activation at SAAC's and address the problem of converting CO_2 to fuels and other useful chemicals (Figure 2) [2].

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Charge transport kinetics at a cathode-solid electrolyte interface studied by μ-cavity electrode

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All-solid-state batteries (ASSBs) are currently accepted as promising candidates for future energy storage devices with conventional layered cathode materials to realize higher energy densities and safe performance compared to flammable liquid electrolyte lithium-ion batteries. However, the interface between the cathode / solid electrolyte still remains a crucial issue that hinders the practical application of solid-state lithium batteries [1]. In typical solid-state batteries, the porous nature of the composite electrode and its porosity, electrode thickness, and uneven distribution of active materials complicate the estimating of the solid-solid interfacial kinetics. Hence, characterizing the interfacial properties of single cathode particles without affecting the above-mentioned parameters is required for fundamental understanding. Previously applied approaches (e.g., single particle measurement) for investigating the interfacial behavior of single active material particles with microelectrode are well adapted for characterization in liquid electrolyte systems and cannot evaluate active particles in combination with solid electrolytes in ASSBs [2]. Thus, the development of novel and sophisticated approaches is required.

The current study investigates the DOD-dependent interfacial charge transfer kinetics between cathode particles and solid electrolytes using a microelectrode with a cylindrical cavity trap. The NCM cathode particles from the prepared dry electrodes are immobilized in the cavity traps by compression on a glass substrate. Further, the as-prepared μ-cavity electrode was transferred to the solid electrolyte system based on the argyrodite-type (Li_6PS_5Cl) solid electrolyte. Several cycles were conducted for confirmation of the stability of electrochemical reactions. In the subsequent cycle, positive and negative pulsed currents were applied after each DOD state, and potential peak responses were measured. The obtained potential peak responses and applied pulsed current amplitudes were used to draw a Tafel plot and estimate the DOD-dependent charge transfer resistance between the cathode / solid electrolyte interface. In general, the charge transfer resistance is often specified in the literature to be equal to the interfacial impedance.

As a result, the study presents an alternative tool to investigate the interfacial charge transfer kinetics between cathode / solid electrolytes in the microscale. The illustration designed μ-cavity electrode in the solid electrolyte system is given in Figure 1. A μ-cavity electrode is a versatile tool and not limited to secondary NCM particles, it is highly adopted for measuring the charge transfer properties of any particles in the microscale by providing the pressure that requires the solid electrolytes.

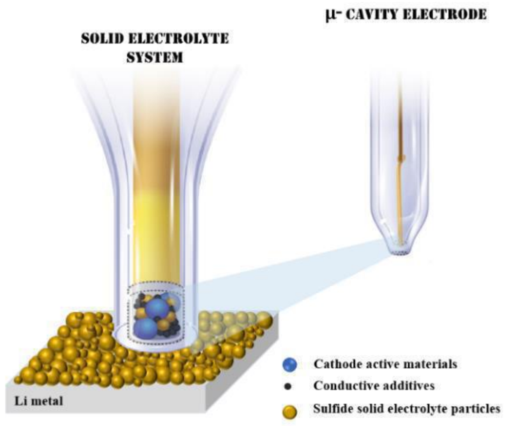

Figure 1. The schematic illustration of μ-cavity electrode in the solid electrolyte system.

The microcavity electrode is an alternative approach for single particle measurement and obtained results can exhibit meaningful clues of charge transfer resistance by Tafel plot and diffusion coefficient calculation for the fundamental understanding of interfacial behavior.

Acknowledgements

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Ionic Liquid Screening for Li-S Batteries

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Li-ion batteries are state-of-the-art energy storage systems widely used in commercial applications such as electric vehicles. However, these battery systems, by nature, cannot fulfill the energy demand in the future. Hence, post-Li-ion batteries, specifically lithium-sulfur (Li-S) batteries, are under investigation. Compared to the 800 Wh/kg specific energy of Li-ion batteries, Li-S batteries possess 2600 Wh/kg specific energy, which is more than three times the former. However, the practical energy densities obtained in Li-S batteries are far from their theoretical values, mainly due to low sulfur utilization and sulfur loss on the cathode side. The polysulfide (PS) shuttle mechanism (PSM), the parasitic shuttling of polysulfides from the cathode to the anode side, is a critical problem of Li-S batteries, resulting in sulfur escaping from the cathode and hence leads to irreversible capacity loss and low Coulombic efficiency. In this respect, preventing PSM is essential to improve the Li-S battery performance [1].

PSM effect is more severe when the concentration of polysulfides is high in the electrolyte; at this condition diffusion rate of PSs will be higher. Because of that, polysulfide concentration should be restricted to decrease the shuttling rate. Many alternatives exist to the most widely used organic electrolytes with high PS solubilities. Among these alternatives, ionic liquids (IL) have gained significant attention recently due to their high chemical and thermal stabilities and tailorable properties [1]. There are thousands of IL structures that depend on the selection of cation-anion pairs, which greatly affect PS solubilities and ionic liquid properties. While low PS solubility of ILs may be advantageous, most ionic liquids have high viscosities, hence low ionic transport. In this respect, selecting an optimum IL is a vital step. Since it is not possible to experimentally test all these ILs, COnductor like Screening MOdel for Real Solvents (COSMO-RS) calculations using COSMOThermX are performed for screening ILs regarding both PS solubilities and IL properties to be used as the liquid electrolytes of Li-S batteries in this study. 98 anions and 370 cations are readily available in the datasets of COSMOThermX, but many others are possible. Hence, using machine learning (ML), the relations between solubility-ionic liquid structural descriptors calculated from density functional theory (DFT) are also investigated to help design ionic liquid electrolytes.

There are 10 structural descriptors of each anion and cation present in the database. Association rule mining results, a commonly used ML method, show the associations between low PS solubility and the levels of each descriptor based on the lift values; high lift values signify stronger associations. As seen in Figure 1, while the level values get higher, higher lift values are obtained. Hence, cations with these descriptors should be utilized in Li-S batteries.

This study shows the importance of the selection of cation-anion pairs of ILs for low PS solubility and viscosities. As seen in Figure 2, COSMO-RS calculations can be used to assess the final capacity retention of Li-S batteries.

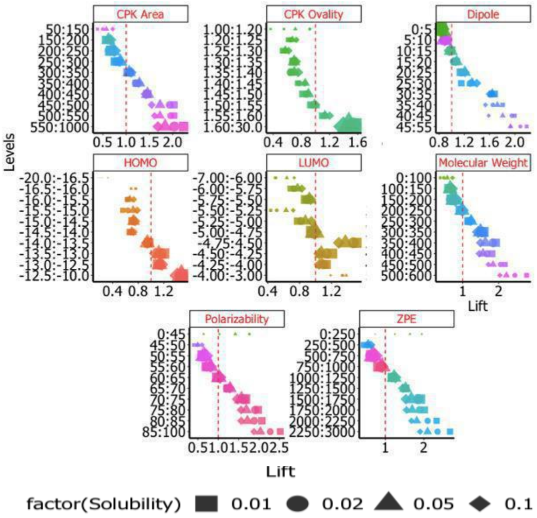

Figure 1. Levels of cation descriptors vs. lift values obtained from association rule mining analysis

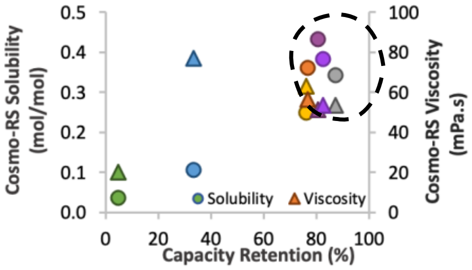

Figure 2. Relation between experimentally measured capacity retention of Li-S batteries vs. COSMO-RS predicted solubility and viscosity values.

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Acknowledgments

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Machine learning analysis of photoelectrochemical water splitting

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Hydrogen is a promising energy carrier and important raw material for the chemical industry[1]. Large-scale hydrogen can be produced by photoelectrochemical water splitting; hence, significnant amount of research has been focused on ways to improve the efficiencies of these systems. This study aims to analyze photoelectrochemical water splitting (PECWS) literature between 2007 and 2020 via machine learning tools. The band gap of the semiconductors and photocurrent density of the PECWS cell were analyzed and predicted using association rule mining, decision trees, and random forest algorithms.

The dataset for PECWS consists of 584 experiments and 10560 data points extracted from 180 articles published between 2007- and 2020. Material properties, PECWS cell details, and operating conditions were used as descriptors, where Band gap (eV) and photocurrent density (mA/cm^2) were target variables.

Models were developed using R. Association rule mining (*apriori*) was used for identifying the influential descriptors on the desired target values (low band gap and high photocurrent density). Decision tree algorithm (*rpart*) was used for the classification of band gap and photocurrent density ranges and the random forest algorithm (*randomForest*) was used for regression. Hyperparameters were optimized using grid search and the best model was selected using cross-validation. Various train-test split ratios (10-40%) and k values for cross-validation (3, 5, and 10) were tried. The complexity parameter (*cp*) was optimized for the decision tree while the number of trees (*ntree*) and minimum split size (*nodesize*) were selected as hyperparameters for random forest algorithm. In all models, it was made sure that the Voltage (bias) - Photocurrent data from one experiment is kept in the same set (validation, train, or test) to prevent information leak from training to testing.

Association rule mining (ARM) analysis for band gap revealed that the anodization method for TiO_2 photoanode resulted in a high band gap. Li and Mo doping for $BiVO_4$ photoanode have a higher probability to give a low band gap compared to other dopants. Decision tree classification of band gap had the cp of 0.1 and accuracy of 0.78 and 0.75 for training and testing respectively. The class accuracy values show that high band gap values can be accurately predicted by the model, hence the rules to avoid high band gap could be trusted.

Figure 1. gives the predictive model developed for band gap using random forest. The best model was found using 40% test splitting and 10-fold cross-validation. The optimum model had *ntree* and *nodesize* of 13 and 35 respectively. The root mean square error of 0.24 and 0.27 were obtained for validation and testing sets respectively.

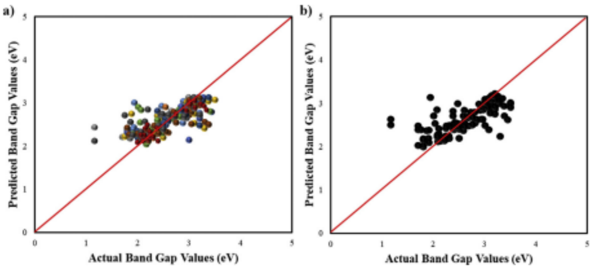

Figure 1. Predicted versus real band gap for a)validation and b) testing sets

Association rule mining analysis of photocurrent density was performed for each of the commonly used photoanodes (i.e. $BiVO_4$, TiO_2, Fe_2O_3, ZnO, and WO_3) separately because the important descriptors for the photoanodes differed. The bias and photocurrent density values were discretized into three categories based on water-splitting domain knowledge and intuition. Influences of each descriptor and their combined effect were obtained for high photocurrent density in low-bias conditions. $BiVO_4$ photoanode tends to have high photocurrent density at low bias when it is doped with Mo, or calcined around 600-700ºC, etc. TiO_2 photoanode doped with C and without any co-catalyst performs well under low bias. Decision tree for the photocurrent density (cp=0.01) model had training and testing accuracy of 0.61 and 0.54 respectively. The overall accuracy was lower than that for band gap classification since this dataset included reaction conditions; the non-standard testing procedure for PECWS may cause noise and decrease performance. Due to similar reasons, a strong predictive regression model could not be developed.

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Machine learning exploration of the bonding in metal hydrides

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Developing novel materials for efficient hydrogen/energy storage and conversion is one of the critical components in the research area of renewable energy resources. The application of machine learning models has been successfully used for some time to select materials with specific properties desirable for hydrogen storage. This study uses unsupervised and supervised machine learning tools to investigate the relationships between crystal structure, bonding properties, and hydrogen storage performance of the selected materials. A collection of over 500 Mg-containing hydrogen storage materials from the Materials Project [1] with the corresponding calculated DFT-level properties is used. Based on the atomic composition, crystal structure of the starting intermetallic compounds, and properties related to the charge density distribution, we address the nature and character of the bonds between the atoms.

The starting point of our research is gathering DFT-calculated charge densities for Mg-containing hydrides using the pyRho python package [2] to help us access and transform the charge density of selected materials. Charge density is the underlying property of DFT and carries information about any ground state property. Charge topology analysis gives us access to many material properties i.e. how can crystal structure be divided into basins corresponding to atoms or how much charge can we attribute to individual atoms. Also, knowing the values of the first and second derivative of the charge density scalar field can give us insight into bonding character between interacting atoms. Variety of important properties like bandstructure, optical response or electrical conductivity of the material are accessed by using charge density as the beginning step.

Figure 1. displays charge density of the MgH_2 [1] that is dominantly governed by ionic cohesion. Numerous researches addressed the influence of alloying or doping on the applicability of various Mg-hydrides. The nature of charge density in those compounds dictates important properties, such as the stability of hydride, band gap… The principal component analysis will be applied to the dataset containing the structural, bonding, physical, and chemical characteristics of these crystals in order to achieve feature reduction. Finally, a machine learning model will be proposed based on the selected input features to correlate intrinsic material properties with macroscopic or application-related characteristics.

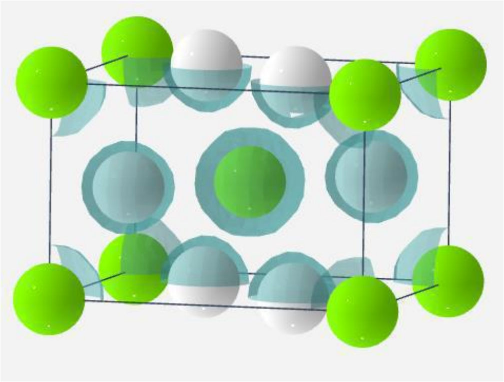

Figure 1. The charge density of MgH_2 [1]. Green spheres – Mg, white spheres – H.

Trends and structure-property relations will be discussed, as well as the possibilities for tailoring the stability of Mg-containing hydrides by alloying based on investigating changes in electronic structure.

Acknowledgments

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Development of MnO_2 Based Cathodes for Alkaline Batteries via Combinatorial Approach

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MnO_2 is a commonly used material in various types of batteries, as it is suitable for electrochemical applications due to its high defect density and structural disorder, including low crystallinity, small crystallite size, unoccupied lattice sites, and foreign cations and molecules within its structure [1]. In addition to its electrochemical properties, it is also abundant in nature and relatively inexpensive compared to other battery materials.

Although MnO_2 is commonly used in primary batteries, there is ongoing research into its use in secondary batteries. The main challenges with MnO_2-based secondary batteries are their reversibility and cycle life due to irreversible reactions [2]. Many elements and compounds have been tested to address this problem, but only Bi has shown significant effects [2,3]. Yadav et al. achieved impressive results with Cu-intercalated Bi-birnessite (layered) MnO_2, reaching 80-95% of the full 2 electron capacity (617 mAh/g) at high loadings and areal capacities for thousands of cycles (>6000 cycles) [4,5]. However, the battery's operating voltage was too low, particularly for the second electron process, resulting in a low energy density.

The objective of this research is to create layered δ-MnO_2 with different compositions using a combinatorial approach in order to identify new compositions that can provide the full two electron capacity at an appropriate voltage value with high cyclic stability. The samples are fabricated using magnetron sputtering with $NaMnO_2$, NiO, Bi_2O_3, and MnO_2 as targets. The thick film cathodes (2-3 µm) are analyzed using cyclic voltammetry and galvanostatic cycling, as well as SEM and XRD.

The samples exhibited varying behaviors, with regions containing high nickel content demonstrating excellent cyclic stability but low capacity and voltage values. Conversely, regions with high bismuth content showed high capacity but acted more like primary batteries. The cathodes with improved electrochemical performance were found to have moderately rich Na content.

Structural investigations showed that preliminery amorphous cathodes as deposited state have been succusfully converted to layered δ-MnO_2 phase during testing.

All the samples showed drastic capacity decay at some point during testing. SEM studies revealed that the thick film coatings lose their integrity and peels off from the surface of the current collector. This is attributed to the volume change of the active material during operation. Preparation of the cathodes via traditional methods may eliminate this problem.

The cathodes tested with a narrow voltage window to speed up the testing of samples. Therefore, their capacities were lower than expected. When a sample from the best performing region is tested for full capacity, a value of nearly 550 mAh/g is reached. However, the capacity wasn't reversible. When the sample is removed from the battery it is seen that the coating was completely removed from the substrate. This may be due to the cathode completely dissolving and the dissolved species moving away, preventing re-precipitation on the substrate. This problem could be addressed by using a gel electrolyte or avoiding complete discharge of the battery.

The improved performance of the cathodes was achieved within a compositional range that is not too distant from $NaMnO_2$ and could be regarded as a doped version of this compound with Bi and Ni cations. $NaMnO_2$ and similar compositions were deemed promising, provided that fragmentation occurring in the cathode, which impairs their full performance, can be resolved through the slurry method with a carefully designed electrode architecture.

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Temperature-Dependent Electrochemical Impedance Spectroscopy (EIS) of Li/MnO_2 Batteries

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Developing next-generation batteries with high energy and power densities requires extensive research into the optimization and characterization of metallic lithium anodes. Metallic lithium has the highest theoretical gravimetric and volumetric energy density compared to other materials, making it an attractive choice for high-performance batteries. Additionally, metallic lithium has a very negative reduction potential, enabling it to store and release energy more efficiently than other materials[1]. Yet, lithium metal anodes are still not commercially available due to a number of problems they face, almost all of them related to the interface between the lithium metal anode and the electrolyte.

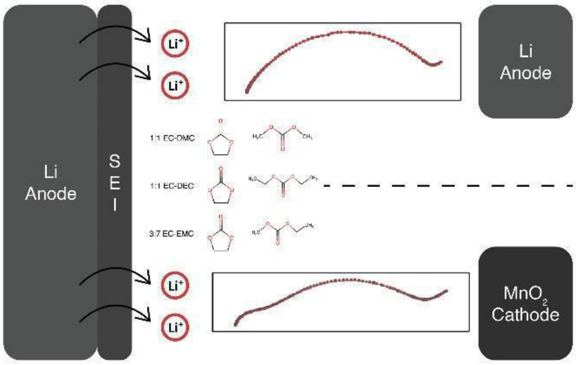

Figure 1. Impedance responses of symmetric and battery-type cells.

Electrochemical Impedance Spectroscopy (EIS), is a non-destructive analysis tool used in electrochemical research. The main principle is applying a sinusoidal excitation voltage (in potentiostatic mode) and analyzing the current response. As the famous Ohm's Law states, voltage is equal to the multiplication of the current and the resistance. The impedance (resistance with alternating current) can be acquired from this equation. In this research, EIS was employed to measure the activation energies of Li^+ transport across the solid electrolyte interface (SEI). EIS facilitates the measurement of critical parameters such as charge transfer resistance, solution (electrolyte) resistance, double-layer capacitance, and mass transport resistance independently in a battery while keeping the battery intact[2]. Measured spectra are fitted with an equivalent circuit fit composed of resistances and capacitors (constant phase elements). These fit values correspond to fundamental processes in the batteries, either belonging to one of the electrodes or the interfaces throughout the battery.

This study utilized EIS to measure batteries with different electrolyte compositions, using 1 M $LiPF_6$ in EC-DMC, EC-DEC, and EC-EMC solutions in Li/Li symmetric cells and Li/MnO_2 cells. The symmetric cells enable the isolation of the metallic lithium electrode on both sides, whereas battery-type cells exhibit a complete anode/cathode behavior. By comparing the two spectra, the effect of the cathode on the impedance response can be investigated. This comparison allows for unequivocal assignments of the various features of the impedance spectra to the phenomena in the batteries. The measurements were taken in a temperature-controlled chamber, ranging from 15°C to 65°C, to determine the activation energy of charge transfer resistance across the SEI. Using the Arrhenius equation, the resistance values obtained were then used to calculate activation energy.

The results demonstrate the dependency of SEI resistance and charge transfer activation energy (E_A) on electrolyte composition and battery architecture. It is also revealed that activation energy is related to the electrolyte compositions and the aging of the cell. Therefore, different electrolytes showed varying impedance results and activation energies.

In addition, the architecture of the cell (symmetric vs. battery-type) also had an impact on the activation energy of the charge transfer through the SEI. The Nyquist and Arrhenius plots of two types reveal the characteristics of the charge transfer.

Further developments in battery engineering will require a deeper understanding of how these electrolytes can affect the SEI and how they change as the battery is cycled. As a result, this study fills the gap in the literature on the SEI investigation concerning electrolyte composition and cell architecture with EIS.

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Can The Fundamental Physical Constants Be Obtained via Fitting Temperature Dependent Nonlinear EIS Data?

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Electrochemical Impedance Spectroscopy (EIS) is a widely used technique in battery technology because it provides crucial insights about what's happening in the battery without damaging it. It can provide information about capacitance, electron transfer rate, Solid Electrolyte Interface (SEI) and other specific details independently from each other. Generally, this technique is done by applying small amplitudes of Alternating Current (AC) within a frequency range of 10 mHz to 1 MHz.

One of the topmost challenges of Electrochemical Impedance Spectroscopy (EIS) is the lack of clarity in data analysis. One of the most used analysis methods is the Equivalent Circuit model fitting which provides information that is model dependent and not unique. Further, analyzing the impact of fundamental parameters such as cathode thickness, particle size etc is almost impossible. Therefore, it is essential to offer a reliable approach to data analysis for EIS.

In 2018, Murbach and Schwartz [1] as a possible solution to the issue of data analysis in EIS, presented a physics-based simulation using a pseudo two-dimensional battery model. They prepared a database containing 38,800 EIS spectra where they used to compare experimental data and match it through a least squares matching approach. While their paper proposed a new method, it still faces challenges due to the problem of multi-matching, which can result in making wrong outputs especially in specific parameter analysis.

The ultimate goal is to develop an EIS analysis method that is grounded in the fundamental principles of electrochemistry. To obtain such an analysis method, it is necessary to get rid of the degeneracies by using temperature dependence and non-linearities as new variables. By defining parameters considering these variables, this method reduces uncertainty and minimizes the potential errors.

Instead of fitting a single impedance spectrum, we propose fitting a set of spectra taken across multiple temperatures along with the information regarding higher harmonics. This approach minimizes the multi-matching problem that Murbach and Schwartz[1] experienced.

We used a physics-based model library on Python called PyBaMM [2] to provide a new approach to EIS data analysis. We simulate voltage as a function of current within a defined frequency range. To overcome the degeneracy problem, we vary the temperature and analyze nonlinearities by looking at the second and third harmonics in frequency domain data. Obtained linear and non-linear voltage simulation data will be compared and tried to fit by using simplex fitting method.

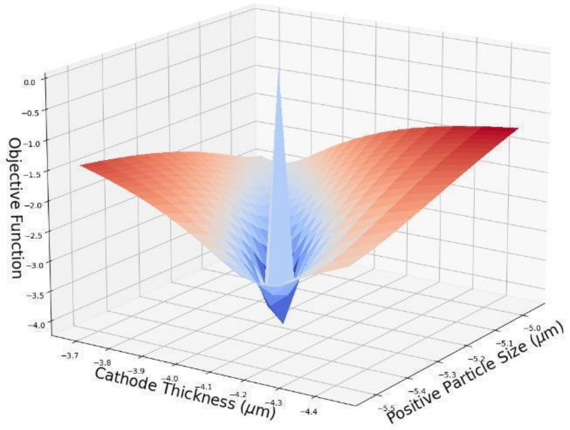

Figure 1. The objective function of Cathode Thickness and Positive Particle size ranging from 35μ to 79μ and 3μ to 11μ respectively.

$$\sum_{T=-25^{\circ}C}^{65^{\circ}C} \frac{1}{N} \sum_{f=100\,\mu\mathrm{Hz}}^{10\,kHz} \frac{(z_r(f,T)-z_{0,r})^2+(z_i(f,T)-z_{0,i})^2}{(z_0)^2} + nonlinearity$$

Here we defined our objective function as where z_0 is the parameters before simulation, N is the number of frequency and z_r,z_i represent real and imaginary numbers of the impedance data. By calculating this over a frequency range and temperature range, the degeneracy will be reduced. To further increase the accuracy of simulation, we will modify and improve this function by adding a non-linearity term in order to obtain a better fitting results in our simulations.

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Electrochemical Noise Investigation of Lithium Anode During Charging Process and Early Detection of Dendrite Formation

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Electrochemical noise analysis is a widely utilized technique in corrosion research, enabling the identification of corrosion modes and differentiation between localized and uniform corrosion types when combined with post-mortem investigations. With the growing prominence of lithium-ion batteries, there is an increasing demand for faster, easier, and more cost-effective testing methods that are non-destructive and non-disruptive. While some studies have explored electrochemical noise measurements in batteries, the existing literature on this topic remains scarce and questionable. By employing electrochemical noise analysis on lithium batteries, it is possible to non-invasively assess battery health. [1] Our previous research has demonstrated an increase in voltage noise in non-rechargeable Li/MnO2 batteries following exposure to short circuits, indicating morphological changes in metallic lithium. This approach offers a potential non-invasive diagnostic tool. [2]

Lithium metal-based chemistries possess significantly higher capacities compared to rechargeable alternatives due to the use of metallic lithium at the anode, instead of lithium-aluminum alloys. Charging lithium metal electrodes can lead to the formation of dendrites, which pose a risk of short circuits, battery combustion, or even explosions by compromising the separator that separates the anode and cathode. Detecting potential dendrite formation beforehand is of great academic and industrial importance. Initial investigations have shown a significant increase in noise levels after charging, accompanied by severe deterioration in the anode as observed through scanning electron microscopy (SEM). Electrochemical noise measurements have shown significant noise level increases during the charging and discharging cycles of lithium batteries, as evidenced by preliminary studies (Figure 1). This observation parallels the noise measurements conducted on non-rechargeable lithium chemistry batteries exposed to short circuits, underscoring the importance of studying noise variations during these cycles in dendrite-prone lithium batteries. Additional preliminary noise measurements on the lithium anode further confirm the rise in noise levels after charge and discharge cycles.

This conference presentation provides an overview of electrochemical noise measurements and explores the underlying causes behind the noise level increases specifically in the lithium anode. To establish correlations between noisy features in the noise measurements and the formation of mossy and dendritic structures during the charge and discharge processes, we will present findings from optical and electron microscopy analyses.

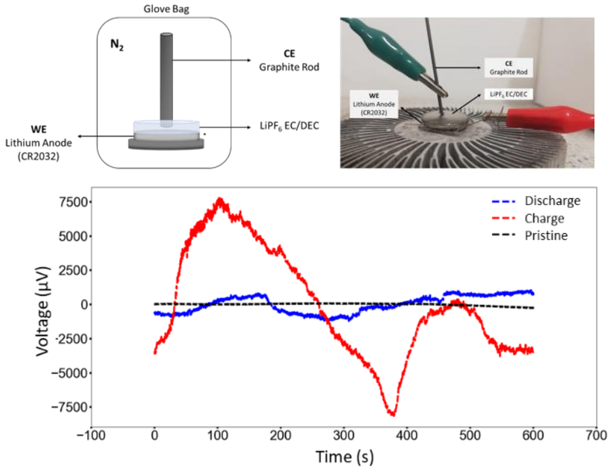

Figure 1. The noise measurement of pristine CR2032 (black) and the noise measurement of CR2032 after charged (red), and discharged (blue)

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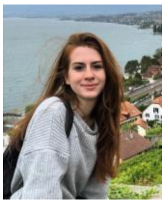

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Temperature and laser power dependencies of $LiCoO_2$ Raman spectra

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Raman spectroscopy is actively used to study the phase and structural changes in lithium-ion batteries electrode materials, since the low weight of lithium ions makes it difficult to quantitatively analyze materials by such methods as X-ray diffraction analysis and energy-dispersive X-ray spectroscopy. Thus, Raman spectrum of lithium cobalt oxide $LiCoO_2$ (LCO), clearly shows a shift of the bands towards lower wavenumbers with a decrease in their amplitude and broadening with deintercalation of lithium ions. A similar behavior of vibrational modes in the spectrum is also observed in the process of heating. Thus, the interpretation of the spectrum of a delithiated sample may be inaccurate, especially due to the possible laser heating of the LCO during measurements.

In this work, we investigated the features of the interaction of laser radiation with individual LCO particles. To do this, we first studied the temperature dependence of the parameters of the LCO Raman spectrum and found that the band shift is described by thermal expansion and anharmonicity. Next, we measured the dependence of the Raman spectrum parameters on the power of laser radiation. The results showed that the shift is more pronounced than during heating and can reach up to 22 cm^{-1} for the E_g and up to 20 cm^{-1} for the A_{1g} mode. In this case, the shift and broadening of the bands turned out to be inhomogeneous for different particles. Using the obtained ratio of the band shift versus temperature for the power dependence, we found that such a maximum shift is equivalent to the shift upon heating to approximately 900°C. Since LCO begins to form cobalt oxide at even lower temperatures, this suggests that this shift cannot be explained by laser-induced heating alone.

The results obtained indicate that, in Raman measurements of LCO, it is necessary to use a low excitation power to avoid degradation of the material and to consider laser heating in the quantitative analysis of the obtained experimental data.

Acknowledgements

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Light scattering geometry for Raman spectroscopy measurements. The case of lithium iron phosphate microparticles

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Raman microspectroscopy is a great tool to study particulate lithium battery materials of micron and submicron sizes. It allows to observe lithium ions deintercalation, to judge the heterogeneity of the sample, etc. But for a proper interpretation of experimental results, it is important to understand the geometry of laser radiation propagation in the object under study as accurately as possible.

Previously, we studied the locality of Raman spectra measurements and revealed a significant optical inhomogeneity for individual particles of lithium iron phosphate $LiFePO_4$ (LFP), a popular cathode material for lithium-ion batteries. The measurements revealed not only the dispersion of the radiation penetration depth for the transparent LFP, but also the enhancement of the signal of the Raman-active silicon substrate under the particle and the blocking of the response at its edges [1, 2].

In the current study, to more accurately interpret the results obtained, we performed modeling in the COMSOL Multiphysics software package and additional vertical Raman mapping of single LFP particles on a silicon substrate.

Although the amplitude of the main characteristic band of silicon substrate (at 521 cm^{-1}) was expected to reach the maximum value aside a particle, the performed measurements have demonstrated mainly the opposite results. Si band amplitude was about 1.5 to 2 times greater being focused on the substate with particle comparing with substrate without one (Figure 1). Response from Si substrate was blocked, but mainly at the particle edges, and this effect varied from particle to particle.

The present study provides insights into the light scattering in LFP single particles underlying the importance of their geometry, which helps to explain heterogeneity of the Raman signal of Si substrate. Also, while there are better techniques for amplifying the Raman signal, the study is relevant for interpreting measurements and understanding the region of signal generation.

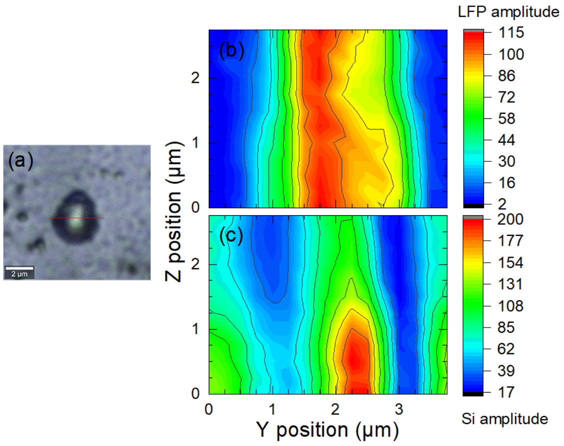

Figure 1. The optical image of LFP particle (a) with corresponding Raman mapping of amplitude of LFP band at 951 cm^{-1} (b) and Si band at 521 cm^{-1} (c) along red line.

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BATTERIES

One-step fabrication of all-in-one flexible nanofibrous lithium-ion battery

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Flexible batteries offer new opportunities to electronic devices making them foldable, bendable, and easily portable. Such qualities can be implemented in wearable electronics, interactive media and medical devices[1]. Flexible batteries can be used as a power source in health monitoring sensors, providing better contact with the human body[2].

The "all-in-one" flexible Li-ion batteries was fabricated by one-stage electrospinning of PVDF-HFP-based precursor solution loaded with active materials, as presented in Fig. 1. Nanostructured graphite and $LiFePO_4$ were used as anode and cathode active materials, respectively. An optimum amount of CNT was added to the electrospinning solutions to increase the electronic conductivity of the fibrous electrodes. The electrochemical performance of the anode and cathode membranes was investigated in lithium half cells. The areal capacities of the electrodes were around 5 µAh cm^{-2} with stable performance for more than 30 cycles. Further, three solutions for the anode, separator (containing polymer only) and cathode were electrospun successively on top of each other. As a result, a flexible, bendable and semi-transparent membrane containing all three components (*i.e.*, cathode, separator and anode) was fabricated. The membrane was then soaked into the liquid electrolyte and assembled into a quasi-dry full-cell battery.

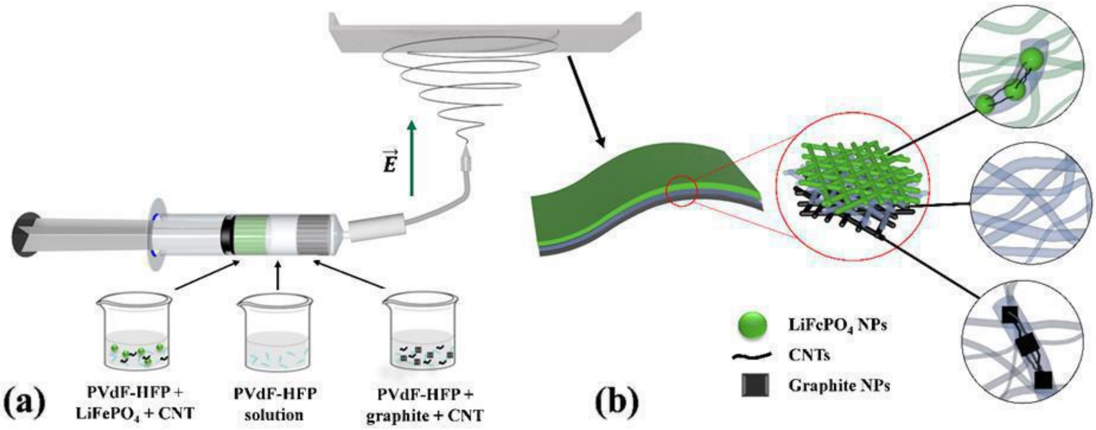

Figure 1 (a) Scheme of one-stage preparation of flexible lithium-ion battery by electrospinning, (b) Schematic illustration of "all-in-one" nanofibrous membrane and its composition

After activating pouch cell by adding the liquid electrolyte, the "all-in-one" battery was tested for bending resistance. The initial voltage of the as-assembled "all-in-one" battery was observed as 0.177 V and after 20 bends it dropped to 0.146 V. During further 20 cycles of bending and folding the battery demonstrated 0.125 V potential.

The developed "all-in-one" membrane assembled within copper and nickel meshes acting as anodic and cathodic current collectors demonstrated semi-transparency. It is enabled by the swollen polymer fibers network, which provides transparent substrate for nano-sized particles of active materials. The thin metallic mesh used as current collectors could maintain the overall transparency of the cell. This work opens the opportunity for developing a new generation of flexible and transparent batteries, since various nanosized active materials can be loaded into the conductive nanofibrous structure.

Acknowledgement

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Development of Room Temperature Na-S and Na-Se Batteries: What Lessons Learned from Li-S Chemistry

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The uncontrolled growth of the world's population and the rapid advancement of technology are leading to ever-increasing energy and environmental problems. In order to find effective solutions to these problems and for a sustainable future, the need for rechargeable batteries with high energy density is increasing day by day. Although most of the work in the literature has focused on sulfur-based batteries, the practical implementation of sulfur-based batteries seems unlikely due to several challenges such as the severe shuttle effect of polysulfides, the low electrical conductivity of sulfur, and significant volume changes during discharge and charge cycles leading to low coulombic efficiency, deteriorated cycle stability and safety issues. On the other hand, selenium-based batteries have attracted significant research interest in recent years and have been recognized as one of the most promising candidates for next-generation energy storage systems due to their characteristics such as higher conductivity under ambient conditions, higher density and comparable volumetric capacity (3253 $mAh\cdot cm^{-3}$) compared to their sulfur-based counterparts.

When it is compared with the sulfur-based batteries, the discharge-charge behaviors differ depending on the type of electrolyte solvent, namely carbonate- or ether-based. While the working principle of Se cathode in ether-based electrolyte demonstrates a stepwise conversion from long to short-chain polyselenide formation, a single-step conversion from Se to the least Se reduction species (i.e., Na_2Se or Li_2Se) is observed in the carbonate-based electrolyte without generation of dissolved polyselenide intermediates [1,2]. However, Se-based batteries are still plagued with several challenges related to the end-products. For instance, regarding Na-Se batteries, the low density of Na_2Se (2.62 $g\cdot cm^{-3}$) leads to drastic volume expansion during complete sodiation (~ 336 %), which deteriorates the structural integrity of the Se cathode during repeated cycles. Another issue raises from the low electronic conductivity of Na_2Se, resulting in low active material utilization and sluggish redox kinetics [3].

Herein, we will discuss potential electrocatalyst (i.e. tetraiodo nickel phthalocyanine (NiPc), Mn_2O_3) to improve the electrochemical performance of Na-Se batteries. It will be demonstrated that the presence of even a small amount of electrocatalyst improves the electrocatalytic conversion of Na_2Se by lowering the decomposition energy barrier of Na_2Se. The improved cell performances are verified by the decrease in reaction polarization, Tafel slope values, and the measured internal resistance of Na-Se cells in addition to the DFT calculations. Consequently, the Na-Se cell with the electrocatalyst exhibited outstanding rate capability, which is one of the most promising rate performance characteristics demonstrated in the literature (Figure 1).

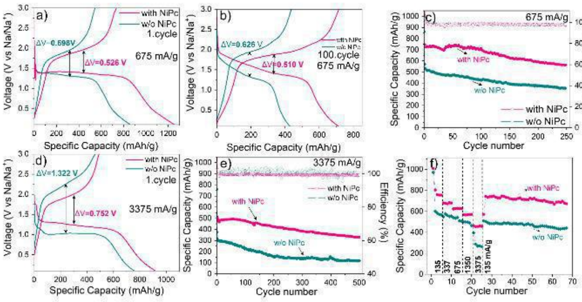

Figure 1. Comparison of the galvanostatic charge/discharge profiles of cathodes with and without NiPc electrocatalyst at 675 mA·g−1 for a) 1.cycle and b) 100.cycle, c) Cycling performance of cathodes with and without NiPc electrocatalyst at 675 mA·g−1 current density, d) Comparison of the galvanostatic charge/discharge profiles of cathodes with and without NiPc electrocatalyst at 3375 mA·g−1 for 1.cycle, e) Cycling performance of cathodes with and without NiPc electrocatalyst at 3375 mA·g−1 current density, and e) Rate performance of the two cathodes at varied current densities. (1 C = 675 mA·g−1)

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An investigation of the cathode electrolyte interphase (CEI) formation of Ni-rich layered materials by Ni ion catalyzation: monolayer CEI formation from an oligomer

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Layered $Li[Ni_xCo_yMn_z]O_2$ (NMC) materials are the most promising cathodes for current use of lithium ion battery owing to the future electronics devices application regarding to their high capacity, low cost, and good cycling. Three transition metal ions in layered materials dominate three main parameters, containing capacity (Ni ion), cycling performance (Mn ion), and good electronic conductivity (Co ion). However, recent research showed that the higher Ni ion content of layered materials suffers surface instability due to cation mixing problem between Ni^{2+} and Li^+ as well as self-reduction of Ni^{4+} leads to rapid capacity fading and gas evolution. Although some studies proposed a coating on NMC surface may overcome aforementioned problems, but surface homogenous and coating thickness become other challenges. Instead of using coating method, this study investigates Ni ion catalyzation mechanisms of NMC materials and propose a monolayer cathode electrolyte interphase (MCEI) formation by maleimide. This MCEI expects to stabilize the surface of NMC that prevents the self-reduction of Ni^{4+} at high temperature operation. The result of this work indicates the MCEI significantly decreases internal impedance of battery. In addition, a great cycling performance under higher rate capacity (195 mAh/g at 1C and 151 mAh/g at 5C) than the pristine. Investigations of the Ni ion catalyzation studies and the MCEI formation offers significant information, which improves battery performance and further design for related accessories.

Professor Fu-Ming Wang was born in Taipei, Taiwan. He received the B.S. and M.S. chemical engineering degree from National Taipei University of Technology (NTUT) and National Taiwan University of Science and Technology (NTUST). He received his Ph. D. degree in electrochemical engineering and lithium battery technology from National Tsing Hua University (NTHU) at 2009. From 2010~2017, he services as a Professor at NTUST and focuses on the researches of lithium ion battery and biosensor.

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Modelling Lithium Transport in Intercalation-type Active Materials Suitable for Transportation Applications

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Lithium-ion batteries are important for the future of transportation sustainability. With the depletion and rejection of fossil fuels, it is clear that mobility will depend ever increasingly on electric vehicles. However concurrent with this increase, is the need to properly evaluate and optimize lithium-ion battery electrode materials, electrolyte composition operating conditions, which include the C-rate and operating temperature, and the cell design in general. This is especially with regard to improving energy density, durability, recharge time and safety. Active materials are used in the electrodes and it is necessary to understand the lithium transport within such materials.

Providing that the discharge of the lithium-ion battery is long and the C-rate is low, then using Fick's Law gives reasonable results. For high-power current pulses however, commonly found in transportation applications, which require short discharge and a high C-rate, using Fick's Law without modification is not appropriate as the assumption has to be made that lithium propagates with an infinite velocity. Also the causality or inertia effect is not taken into account at short-time scales which means the lithium flux develops instantaneously with lithium concentration gradient.

In this work Fick's Law is used to calculate lithium transport within intercalation-type active materials but use is also made of the Maxwell-Cattaneo-Vernotte (MCV)[1] theory which captures the impact of lithium transport inertia on the electrochemical response of materials. The theory should take into account finite speeds. For the concentration gradient of a chemical species, a similar MCV equation is used here, which is hyperbolic, and does not have infinite speed propagation, hence keeping the transients finite.

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Prof. Zhumabay Bakenov received his Doctor of Engineering from Tokyo Institute of Technology, Japan. He is currently a Professor of Chemical and Materials Engineering at Nazarbayev University in Kazakhstan and also serves as a Director of Center for Energy and Advanced Materials Science of National Laboratory Astana. His research focuses on new materials for next generation energy conversion and storage.

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The formation of residual Li compounds on Ni-rich NCM cathodes and their effect on the electrochemical performance in LPSCl-based ASSBs

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Nickel-rich $LiNi_xCo_yMn_{(1-x-y)}O_2$ (NCM-type) lithium transition metal oxides have attracted a significant interest as a cathode material in lithium ion batteries due to their high energy density and low cobalt content, however, their reactivity with air during storage/handling and how this affects the electrochemical performance had been overlooked until the recent years. Exposure to air (which consists of H_2O and CO_2) during storage/handling can lead to formation of LiOH, $LiHCO_3$, Li_2CO_3 and also basic transition metal hydroxides/carbonates.**[1,2]** The formation of such residual lithium compounds can also cause structural changes near the surface of cathode particles after leaving highly delithiated regions.**[3]** Therefore, it is crucial to understand how such residual lithium compounds are formed during the synthesis and post-synthesis storage. It is also very important to understand how these compounds affect the electrochemical performance.

In all-solid-state batteries (ASSBs), the presence of Li_2CO_3 can positively affect the electrochemical performance in sulfide-based solid electrolytes,**[4,5]** however, there has been no dedicated study which aimed to understand relationship between the cell electrochemical performance and the presence of residual lihium compounds -with a focus on the type of compounds present. In this study, we prepare $LiNi_{0.83}Mn_{0.06}Co_{0.11}O_2$ single crystal powders with different residual lithium amounts and types, by either carefully controlling the washing procedures, or post-processing conditions (e.g. heat treatment parameters). The ambient air exposure conditions (e.g. with different humidity and CO_2 concentrations) are further used to change surface properties of powders during storage. Alternatively, NCM powders were also coated with lithium compounds such as Li_2CO_3 using external lithium sources. Characterization of such NCM powders will be presented in this talk. Valuable insights which we gain from a number of analytical techniques such as XPS, TOF-SIMS, TGA-MS, FIB-SEM, acid titration and XRD will be presented. Later, the relationship between the residual lithium compound type (and amount) and the electrochemical performance will be discussed (in ASSB cells with LPSCl-based sulfide solid electrolyte).

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Direct Electroplating of Active Materials for Batteries: No Binder, No Carbon, No Slurry Processing

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Electroplating method has been utilized to obtain anode active materials for next generation lithium ion batteries (LIBs). Both cathode and anode active materials can be directly obtained via electroplating avoiding the energy and time consuming steps i.e. powder synthesis, slurry preparation, electrode production. Skipping these steps can revolutionize battery industry and create a large profit.

In order for electroplating to be continues relatively speaking a good electrical conducting materials need to be considered. For this, in this talk we aim to discuss the direct electroplating for the following materials: i-) $LiCoO2$ cathode active material, ii-) Tin anode active material iii-) Silicon anode active materials. For the latter, the Si is not a good electrical conductor so we also will focus on how to overcome loading limitation on these materials. Both aqueous and non-aqueous based electroplating methods will be elaborated during the talk and will give a holistic picture of where our researches are centered.

The talk will also dive in to how electroplating can bring different approaches for decreasing the cost of precursor of the active materials by allowing low purity precursor utilization. Current state of the art cathode producers have to use up to 99.9% purity Lithium, Cobalt and Nickel precursors regardless of precursor types such as hydroxides, nitrates or carbonates. Here with our approach we showed that we can achieve high purity cathode active materials, i.e. LCO, with utilizing super low purity of LiOH and $CoOH_2$ allowing a significant cost reduction.

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Effect of Transition Metal Doping on the Electrochemical Performance of NCM811 Cathodes

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Ni-rich $LiNi_xCo_yMn_zO_2$ (NCM) cathodes have been the subject of considerable research due to their high capacity and potential application in lithium-ion batteries for electric vehicles. Among these materials, $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM811) has emerged as a promising candidate for next-generation energy storage solutions [1]. However, the intrinsic structural and cycling stability issues associated with Ni-rich cathodes necessitate the development of effective strategies to enhance their performance and longevity. Doping with extrinsic multivalent cations has been established as a viable method to address the stability concerns of Ni-rich NCM cathodes. In light of this, our study presents a comprehensive investigation of developing an efficient screening methodology for doping NCM811 cathodes with a range of cations, including Mg^{2+}, Al^{3+}, Ti^{4+}, Zr^{4+}, Ta^{5+} and W^{6+}[2, 3].

The methodology is founded on a "top-down" approach, whereby a precursor layer containing the dopant is coated onto the cathode material, followed by the diffusion of the dopant into the particles during heat treatment at elevated temperatures. This approach facilitates the rapid identification of potential dopants for Ni-rich cathode materials, paving the way for further optimization and realising high-capacity, stable cathode materials. Furthermore, the research delves into the impact of the oxidation states of the dopants on the electrochemical, morphological, and structural properties of the Ni-rich NCM cathodes. Through a series of galvanostatic cycling measurements, it is observed that cathodes doped with high oxidation state dopants, particularly Ta^{5+} and W^{6+} display superior performance compared to their undoped counterparts and those doped with low oxidation state dopants [2, 3]. Additionally, physicochemical measurements and analyses reveal distinct differences in the grain geometries and crystal lattice structures of the various cathode materials, which contribute to their diverse electrochemical performance characteristics and correlate with the oxidation states of their dopants.

Taken together, the findings of this study offer valuable insights into the role of dopant oxidation states in the enhancement of Ni-rich NCM cathode materials, as well as a streamlined method for identifying suitable dopants for high-capacity, stable NCM811 cathodes. Ultimately, this research has the potential to significantly advance the development of high-performance lithium-ion batteries for electric vehicle applications, thereby contributing to the broader goals of energy sustainability and environmental conservation.

Acknowledgement

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Study of the electrochemical properties of high voltage $LiCoPO_4$ cathodes via solution combustion synthesis

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Olivine-type cathode materials are preferred due to the advantages of their orthorhombic (Pnma) crystal structures. Among these, $LiFePO_4$ (LFP) is an example that is widely used commercially. In addition to its good electrochemical properties, LFP is a cyclically stable, safe, economical, and environmentally friendly material [1]. However, since LFP's voltage potential is limited to 3.2 V, it has limitations in competing with oxide-based cathode materials in a layered structure in high energy density areas such as electric vehicle technology. For this reason, there have been searches for alternative olivine-type cathodes having high energy density. Cathode materials in an olivine structure have been produced using different transition metals instead of Fe. For example, when elements such as Mn^{2+}, Co^{2+} and Ni^{2+} are used instead of Fe^{2+} transition metal, the redox potential of the $LiMPO_4$ (LMP) compound was observed to increase to 4.1 V, 4.8 V, and 5.1 V, respectively [2]. The increase in the cut-off voltages of LMP compounds to these values has made them suitable for use in applications requiring higher energy.

However, phospho-olivine-type components have poor electronic and ionic conductivity because of their crystal nature, which results in limited reversible electrochemical performance. In particular, various approaches are used to solve the electrical conductivity problem encountered in olivine-type cathode materials, such as doping, grain size reduction, and coating of particle surfaces with various carbon sources [3].

Combustion synthesis is an effective technique widely used in synthesizing olivine-type LMP cathode materials to combine the approaches mentioned above to improve electronic conductivity. The fuel type and ratio are essential considerations in combustion synthesis, as they affect reaction conditions, stoichiometry, impurity formation, and ultimately the quality and properties of the synthesized LMP material [4].

In this study, we conducted preliminary experiments on synthesizing the $LiCoPO_4$ (LCP) cathode using combustion synthesis to achieve an olivine-type structure, smaller grain size, and desired electronic conductivity. Various fuels such as citric acid, glycine, and urea and their combinations were used to obtain the desired surface coating of the cathode with carbon. The crystal structure of the synthesized active materials of the LCP cathode was investigated using XRD, and the results are shown in Figure 1. The fuel choice affects the phase composition and impurities inthe LCP synthesis process. Although using citric acid promotes the formation of a pure LCP phase, a sufficient capacity could not be obtained in electrochemical tests because the desired carbon coating did not occur on the cathode surface. When glycine was used instead of citric acid, the formation of the Co_2P and $LiCoO_2$ phases was observed. Subsequently, citric acid, glycine and urea were mixed in appropriate amounts, and the peak intensity of Co_2P and $LiCoO_2$ was observed to be reduced.

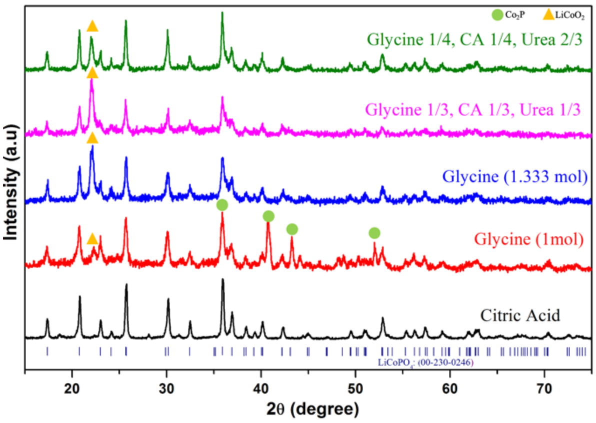

Figure 1: XRD analysis of the $LiCoPO_4$ synthesized using different fuel ratios.

Acknowledgements

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Mixed Niobium Phosphates as Negative Electode Materials for Metal-ion Batteries

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With the rapid development of electric vehicles and energy storage devices safety and powerful requirements to metal-ion batteries becomes apparent. Niobium-containing compounds [1] attracts attention of researchers as negative electrode materials due to their ability to multielectron reactions. They are important for achieving high capacity. High columbic efficiency on first cycle, rate capability and safety are main benefits of Nb-containing anode materials, which distinguish them against the carbon materials, however, there are only a few recent works that are devoted to investigation of niobium phosphates as electrode materials [2,3]. Electrochemical activity of mixed niobium-vanadium phosphates has not been studied yet. Potential of V^{3+}/V^{2+} is located between $Nb^{5+/4+}$ and $Nb^{4+/3+}$ potentials [4], this way three electron red-ox process in low potential area can be achieved.

The aim of this work is research of multielectron redox processes in mixed niobium-vanadium phosphates with NASICON-related structures.

$LiNbV(PO_4)_3$ (*Pbcn*) and $NaNbV(PO_4)_3$ (*R-3c*) were synthesized by sol-gel method, cell parameters of both phases are in agreement with literature data [5]. This method helped us to reduce synthesis temperature and obtain particles with lower size, than once received via solid state route [2]. Morphology is very important for further electrochemical measurements. *Operando*-XANES spectroscopy of $LiNbV(PO_4)_3$ and $NaNbV(PO_4)_3$ proved, that in initial phase oxidation state of Nb is +5. Shift of Nb K-edge during the intercalation processes indicates Nb reduction deeper than Nb^{+4}. Capacity is very close to theoretical, in combination with XANES data it allows us to speculate about the intercalation of 3 alkali cations per formula unit. $NaNbV(PO_4)_3$ demonstrates excellent rate capability up to 10C (more than 80% of theoretical capacity) and good cycling stability (less than 7% capacity fade after 100 cycles) [6]. *Operando* and *ex situ* XRD proved that intercalation processes in both phases are reversible. For $LiNbV(PO_4)_3$ lithation proceeds with single-phase mechanism, with increasing of parameters *a* and *c* and decreasing of parameter *b*. Data analysis obtained from $NaNbV(PO_4)_3$ operando XRD showed the existence of two-phase regions and nonmonotonicity in changing *c* parameter which can be related to activity of different redox processes at different potentials.

Combination of mild chemistry methods and activity of three redox couples allowed to synthesize negative electrode material for high power and long-life metal-ion batteries.

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Improving the performance of Li/graphite half-cells at low temperatures through the modification of electrolyte

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The automotive industry has increasingly favored lithium-ion batteries (LIBs) with high energy density as a reliable source of power for electric and hybrid electric vehicles. LIBs have become an attractive energy storage option due to their high energy density, minimal self-discharge, negligible memory effect, high open circuit voltage, and long lifespan. Despite their advantages, experts worldwide are working to address potential concerns associated with their use, including their performance under different environmental conditions. One such condition is low temperature, which can cause significant capacity loss and rapid self-discharge in LIB-powered devices [1-3].

Researchers are still debating the main reasons for the drop in performance of lithium-ion batteries (LIBs) at sub-zero temperatures. Several studies have concluded that the ionic conductivity of the electrolyte does not have a significant impact on battery performance in cold temperatures since electrolytes with the same conductivity can exhibit different low-temperature characteristics. Instead, the slow desolvation at the liquid-solid interface, reduced lithium migration in the active material, and the formation of an unfavorable solid electrolyte interface (SEI) layer are believed to be the primary factors contributing to this problem. The high energy barrier of Li^+-desolvation on the electrode surface causing significant charge-transfer resistance has been identified as the primary cause of reduced discharging capacity when the temperature drops below 0 °C [2, 3].

Graphite has been the primary material used as the anode in LIBs for several decades now due to its high theoretical specific capacity of 372 mAh g^{-1}, which makes it a desirable choice for negative electrodes of LIBs. However, at temperatures below -20°C, the capacity of graphite is only 12% of its room temperature capacity. The low-temperature electrochemical performance of LIBs is mainly hindered by factors such as difficult Li^+ ion intercalation into graphite, high Rct between the electrode and electrolyte interface, reduced SEI conductivity, and reduced Li^+ ion diffusivity within graphite sheets.

The electrolyte in LIBs consists of lithium salts and solvents, which play a crucial role in the battery's performance. The type of solvent, its compatibility with lithium salt, melting point, dielectric constant, and viscosity have a significant impact on the battery's operating temperature. However, currently available commercial carbonate-based electrolytes have high liquid-solid transition temperatures, making them unsuitable for use in cold environments. To address this issue, researchers have attempted to modify the electrolyte's composition using various methods such as enhanced solvent mixtures, new co-solvents, electrolyte additives, new electrolyte salts, and a combined approach to increase the cell's resistance to low temperatures and widen the operating temperature range of the battery. The best results have been achieved through a comprehensive solution that involves the modification of both the salt and solvents in the electrolyte composition.

In this work, the authors aimed to develop an optimal electrolyte system for the Li/graphite half-cell that can operate under low temperatures by applying a complex modification of the lithium salt and solvents. Various concentrations of commercial and alternative lithium salts were mixed with a combination of solvents to identify the optimal interaction with a graphite electrode at room and low temperatures, and the electrochemical and physical properties of cells using the newly designed electrolytes were studied in contrast to commercial electrolyte.

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Correlation between volume expansion and electrode density of Si-Alloy@Graphite composite anode: In-situ Dilatometry Study

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Recently, Si-based anode materials, including alloys, have been intensively studied to replace low-capacity commercial carbonaceous materials (e.g., graphite). However, they are hindered by their low electronic conductivities and huge volume expansion upon the lithiation/de-lithiation process. For the practical application of Si, Si-graphite blending materials were introduced to compensate for the limitation of Si via an easy and simple blending approach [1]. Nonetheless, when it comes to considering volumetric energy, Si blending with graphite composite electrode swelling is one of the most critical factors to be addressed. To achieve high volumetric energy density, the electrode is calendared under high pressure, leading to a decrease in the electrode porosity. Notably, the porosity of the electrode affects electrolyte penetration, capacity fading, rate capability, side reactions caused by the SEI layer and lithium plating, and mechanical degradation due to the charging stress [2,3]. Thus, studying the relationship between electrode density and volumetric energy by controlling electrode swelling is necessary to achieve high energy density and stable electrochemical properties because, without densification of the electrode, the volumetric energy density of the Si@Gr composite electrode is inferior.

The current research investigates the influence of electrode density on electrode swelling of graphite-blended Si-alloy anode via *in situ* measurement of the electrode swelling with electrochemical dilatometry. To study the swelling behavior of the electrode at various electrode densities, single-layer pouch cells were proposed with the same electrodes: NCM523 cathode vs Si-alloy@G anode. Volumetric energy densities were estimated depending on the electrode swelling at various electrode densities. The amorphous Si-alloy was synthesized using a high-output and mass-producible melt-spinning process; then, the as-prepared ribbon is annealed at a certain temperature (by adopting recrystallization phenomena) to homogeneously crystallize and achieved nanosized-Si (n-Si) embedded in an inactive alloy matrix. The crystal structure, microstructure, and grain growth of Si-based alloy were systematically studied via high-temperature X-ray diffraction (HT-XRD) and focused ion beam combined scanning transmission electron microscopy (FIB-STEM).

The results exhibit a tendency that an increasing the high electrode density provokes higher electrode expansion and contraction as well. The expansion/contraction of the Si-alloy@G electrode depending on the electrode density is given in Figure 1. These tendencies indicate that the porosity of the electrode has a significant effect on the electrode swelling.

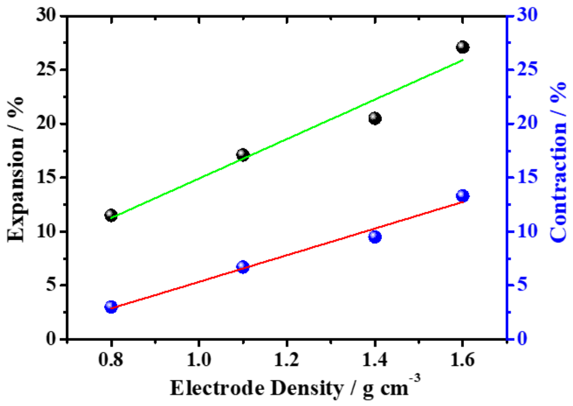

Figure 1. The electrode expansion/contraction versus electrode density in Si-alloy@G electrode.

The results of the study provide an understanding of the importance of optimizing the electrode density to control the volume expansion and achieve a high volumetric energy density of Si blended graphite composite anodes.

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Synthesis of Ni_2P/C nanofibers as anode materials for lithium-ion batteries

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Transition metal phosphides as anode material for Lithium-ion batteries had widespread attention due to their lower polarization, larger capacity and good cycling behavior [1-3]. Moreover, the higher theoretical capacity of Ni-P systems according to their phosphorus number makes them more attractive compared to oxides or sulfides. In this work, Ni_2P/C nanofibers were synthesized using a water-soluble carbon source polyvinylpyrrolidone (PVP) and cost-effective electrospinning method. This work studied the impact of drying temperature on physical and electrochemical characteristics of the electrospun nickel phosphide nanofibers.

The Ni_2P/C nanofibers were synthesized via an electrospinning machine using PVP, nickel nitrate hexahydrate, and phosphoric acid as precursors. The nanofibers were spun at 18 kV voltage and 0.8 mL h^{-1} flow rate. The electrospinning humidity (RH) varied between 20-35%. Obtained nanofibers were dried at different temperatures between 110-130 ºC for 11 h. Finally, prepared fibers were annealed at 700 ºC for 1 h with a heating rate of 5 ºC min^{-1} in the $N_2 + H_2$ (4%) atmosphere.

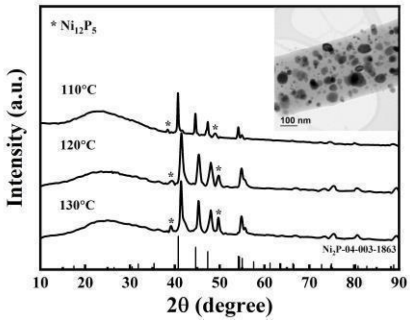

Figure 1. XRD patterns of nanofibers prepared at RH of 25% at different drying temperatures after heat treatment. İnset: TEM image.

The morphology and crystalline phases were observed using X-Ray diffraction (XRD, Miniflex, Rigaku). The microstructure was studied by transmission electron microscopy (TEM). According to the results, Figure 1, Ni_2P with a hexagonal structure and the space group of P62m and $Ni_{12}P_5$ with a tetragonal structure, space group of 87:I4/m were formed regardless of difference in process parameters. TEM results show that nanoparticles are uniformly distributed within the fibers.

The electrochemical characteristics of Ni_2P/C nanofibers were studied using coin-type cells (CR2032) with Li and polypropylene separator under Ar gas (99.9995% purity) in Glove box using 1 M $LiPF_6$ dissolved in a mixture of ethylene carbonate, diethyl carbonate, and ethyl methyl carbonate in 1:1:1 vol. ratio as electrolyte. Assembled cells were tested in a potential range of 0.01–3.0 V vs. Li/Li^+ at a current density of 100 mA g^{-1}. The current densities were calculated based on the mass of the samples which varied between 1.1-1.2 mg cm^{-2}. As a result, the highest initial charge capacity of 710.9 mAh g^{-1} with initial Coulombic efficiency of 61%, retaining a high capacity of 590.7 mAh g^{-1} after 100 cycles was achieved for the best sample.

Acknowledgements

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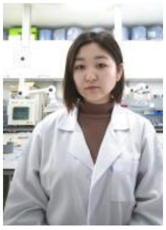

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Synthesis of tin phosphide/phosphate carbon composite nanofibers as low-temperature anode for lithium-ion batteries

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Graphite anode is admitted as one of the critical limiting factors for applying lithium-ion batteries (LIBs) in low-temperature (LT) environments [1]. As an alternative, tin compounds, such as SnO_2, exhibit much better LT performance owing to the unique allotropic changes of tin and increased reversibility of lithiation-delithiation reactions at low temperatures [2]. However, to the best of our knowledge, LT performance of other tin compounds as anode for LIBs has not been reported so far.

In this work, free-standing carbon composite nanofiber mats of tin phosphide/phosphate have been successfully synthesized by electrospinning with heat treatments and applied as anode materials for LT LIBs.

First, the electrospinning solution was prepared by mixing polymer solution (PVP dissolved in ethanol) with precursor solution (different amount of tin (II) chloride dihydrate and phosphoric acid dissolved in ethanol:water (1:2 vol.) mixture). Next, the prepared suspension was electrospun on a NE300 electrospinning machine (Inovenso) at 20-22 kV with a flow rate of 0.8 mL h^{-1}, collected on a drum collector rotating at 100 rpm, and placed 10 cm away from the tip of the needle. Uniform fiber mats were dried at 150 ºC for 12 h, stabilized at 280 ºC for 4 h in the air oven, and further annealed at 700 ºC for 1 h in the flowing Ar + H_2 (4%) atmosphere.

Figure 1a shows XRD pattern of the designed material, which corresponds to tetragonal Sn with a space group of I41/amd and tetragonal SnP with a space group of I4mm. A broad bump between 20º and 30º may indicate presence of amorphous Sn_xPO_4. As seen from TEM image, tin phosphide/phosphate nanoparticles (d = 5–10 nm) are uniformly distributed within carbon fiber matrix (d = 100–150 nm).

The temperature-capability of the 1:1 sample at 100 mA g^{-1} is shown in **Figure 1b** in comparison to the commercial graphite anode. The developed electrode maintains about 200 mAh g^{-1} capacity even at -30 ºC, while commercial graphite completely loses its lithium storage capability at -20 ºC.

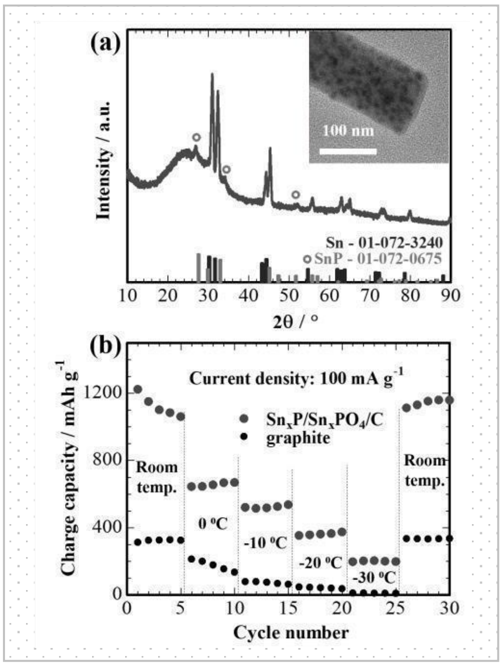

Figure 1. XRD patterns (a) and temperature-capability of the designed material. Inset: TEM image.

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SnSe anode materials for low temperature lithium-ion batteries

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Low-temperature operation of lithium-ion batteries remains a challenge due to the reduced mobility of Li ions and enhanced resistance [1]. Recently, some materials have demonstrated promising results, and among them, we are studying tin selenide (SnSe) anode materials prepared via the electrospinning method.

Tin selenide (SnSe) shows promise as an anode material for energy storage due to its high theoretical capacity and low potential plateau, which can result in higher energy densities and improved cycle stability compared to traditional graphite anodes. SnSe is also environmentally friendly, thermally stable, and relatively inexpensive, making it a practical choice for large-scale energy storage applications [2].

The prepared material was used as an anode material for lithium-ion batteries operating at low temperatures up to -20 °C. SnSe electrode demonstrated an initial discharge capacity of 870 mAh g^{-1} at a current density of 100 mA g^{-1}. Moreover, at a temperature of -20 °C, the electrode exhibited a discharge capacity of 445 mAh g^{-1} at a current density of 100 mA g^{-1}. The outstanding electrochemical performance of SnSe anodes in low-temperature conditions could be linked to the improved conductivity with the addition of carbon and reduced volume changes during charge-discharge processes.

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The buckwheat-derived hard carbon as anode material for lithium-ion batteries

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Lithium-ion batteries (LIBs) that utilize hard carbon(HC) as an anode material have gained significant attention in recent years. HC offers advantages such as higher capacity, wider electrochemical potential window, and better cycling stability, making it an attractive choice for improving the performance of LIBs.

Biomass-derived HC has gained interest as a sustainable and renewable alternative to traditional carbon sources [1, 2].

Nevertheless, it is necessary to strive for a cost-effective option for obtaining HC from biomass.

One of the solutions to this problem is to obtain hard carbon from waste biomass. Buckwheat is a nutritious and versatile crop that is grown in many parts of the world, including Asia, Europe, and North America. Despite its many health benefits, such as being high in protein, fiber, and minerals, buckwheat is often underutilized compared to rise and may be subject to waste.

Herein, we obtained the hard carbon from waste buckwheat seeds for further use in LIBs via pyrolysis in the N_2 atmosphere at different temperatures – from 500 to 1000 °C for 2 h. From Fig.1, it can be seen that almost all samples have both open and closed pores with different sizes from 350 nm to 15 μm.

The electrochemical performance of the hard carbon as anode materials in LIBs was tested in CR2032 coin cells using a lithium metal foil as the counter electrode within the operating voltages of 0.01 to 3.0 V at a scanning rate of 0.1 mV s^{-1}.

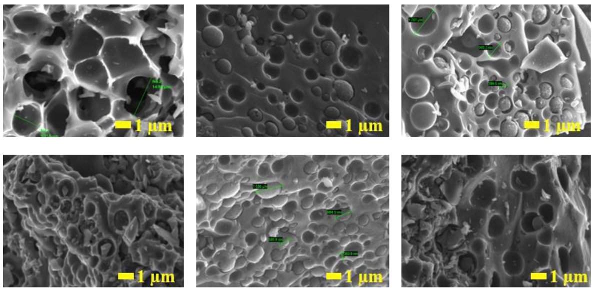

Figure 1. SEM images of obtained HC at different pyrolysis temperatures

The initial discharge and charge capacity for all LIB cells was on average 1200 mAh/g and around 525 mAh/g, respectively. It was found that HCs obtained at different pyrolysis temperatures demonstrated similar electrochemical performances. Nevertheless capacity stability is observed at higher temperatures. The other results including their dependencies on the morphology and composition details will be discussed at the conference.

This study demonstrates the use of waste buckwheat seeds as a sustainable feedstock for the synthesis of HC offers a promising pathway towards the development of high-performance and environmentally friendly energy storage devices.

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Currently, I am a junior researcher at the Institute of Batteries LLC. My research aimed to create new methods of obtaining hard carbon from waste biomass exploring various pyrolysis temperatures, activation methods to produce hard carbon with distinct morphologies and electrochemical properties. In my free time, I like to walk, to notice the beauty in the Botanical Garden in Astana city, reading Kazakh literature and about Islam,

The formation of carbon fiber with embedded red phosphorus nanoparticles as an anode for li-ion batteries

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The increasing demand for high-performance energy storage devices has driven the search for new and innovative electrode materials with superior electrochemical properties. Red phosphorus (RP) has gained significant attention as a promising anode material for lithium-ion batteries due to its high theoretical capacity, low cost, and abundance. The theoretical capacity of RP is about 2596 mAh g^-1, which is much higher than that of commonly used graphite anodes (~372 mAh g^-1). Therefore, RP has the potential to greatly increase the energy density of lithium-ion batteries (LIBs). However, the practical application of RP is hindered by its poor conductivity and large volume expansion during cycling, leading to severe capacity fading and structural instability.

To overcome these issues, various strategies have been proposed to enhance the electrochemical performance of RP, such as nanostructuring, surface modification, and composite formation.

One effective approach is to embed RP nanoparticles in a carbon matrix, which can effectively address the volume change issue and facilitate fast electron and ion transport, resulting in enhanced electrochemical performance. The carbon matrix can also provide good mechanical support to prevent the aggregation and detachment of RP nanoparticles during cycling

In this study, we report the simple synthesis and characterization of obtaining RP nanoparticles which are embedded in porous carbon nanofibers (polyvinylpyrrolidone) by electrospinning method. During the preparation process the different parameters were varied such as red phosphorus particle milling parameters (time and ratio), solution concentration, nanofiber coating parameters (speed, voltage and distance to the collector) and annealing parameters (temperature and atmosphere). A schematic illustration of nanofiber production is shown in Figure 1. The resulting red P@C nanofiber was evaluated as freestanding or conventional anode material for LIBs, and their electrochemical performances were compared to that of pure carbon nanofibers. Our results demonstrate the potential of the red P@C nanofiber composite as a high-performance anode material for energy storage applications. The other characterization and test results will be presented and discussed at the conference.

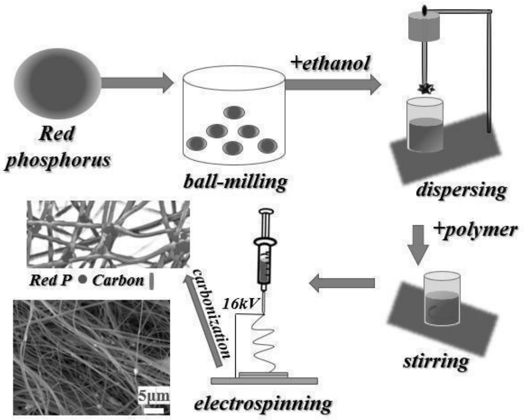

Figure 1. Schematic illustration of the preparation process for red P@C nanofibers.

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Yelnury Baltash, young researcher. She completed her master's degree in a two-degree program (Kazakhstan and Russia) in chemistry. She works as a Junior Researcher on the project "Development of composite anodes based on red phosphorus for the next generation of lithium-ion and sodium-ion batteries" at the Institute of Batteries. Her scientific interests include obtaining new composite anode materials with improved electrochemical characteristics, search and realization of new methods of anode formation.

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Exploring tailored carbon-coated tin nanomaterials as anode for Li-ion batteries

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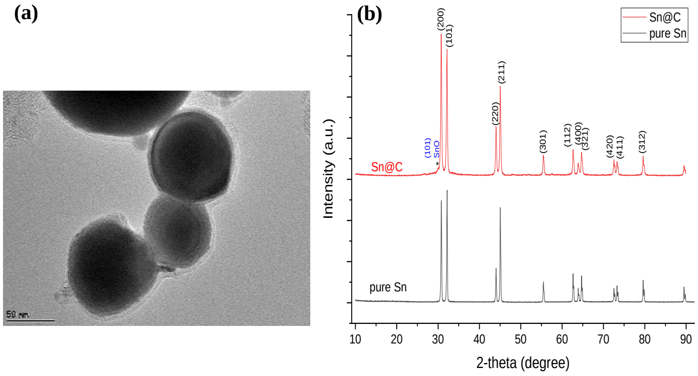
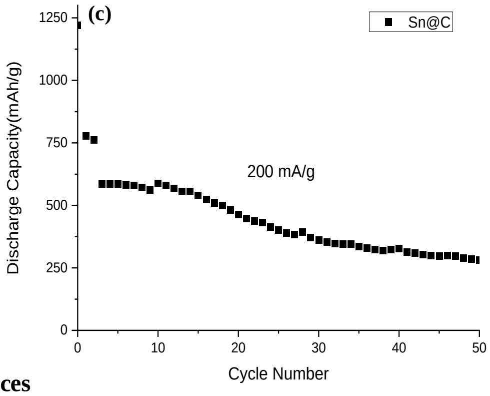
Lithium ion batteries, one of the most promising candidates to store electricity in wide scale, have been dominated many industrial fields, such as portable electronic devices and electric vehicles due to its relatively high energy density and good rate capability. To meet the further increasing demand for energy storage capability, novel electrode materials with higher capacity, low cost, and the ability to be produced at large scale are of great interest. Based on the alloying reactions with Li ions, Sn and Sn-based compounds are strong anode materials intensively researched due to their much higher energy capacity than that of commonly used intercalation-type graphite anode. However, the insertion of lithium atoms per Sn atom has some challenges which have hindered their widespread use. The full lithiation of Sn results in a huge volume change (~400 %). This dramatic volume change can result in fragmentation and leads to loss of electrical contact between active materials and electrode framework, which causes significant capacity fading, and thus, deteriorated battery performance. Currently, in order to overcome these problems, using the nanoscaled active materials and combining them with carbon structures are two most studied approaches for alleviating the volume expansion problem, which adopts to the large volume change and increase the interfacial area of contact between electrodes with electrolyte, and provides enormous conductivity by means of carbon matrix.[1,2]

The current study includes the production with a unique approach that allows to prepare Sn nanoparticles with designed carbon interfaces (Sn@C) as anode electrode for Li-ion batteries using RF induction thermal plasma reactor. Thermal plasma is widely used nanoparticle synthesis technique because of having high purity, versatility and scalability material processing compared to the alternative techniques. TEM images of the powder in Figure 1a display that a range of structures including core-shell particles are crystal Sn nanoparticles successfully encapsulated with very thin amorphous carbon shell produced by thermal plasma reactor. Average size of these particles are about between 50 and 100 nm and the thickness of carbon shell is the range from 10 to 20 nm. Additionally, forming free Sn/SnO nanoparticles and graphite with spherical nanoparticles are inevitable. The electrochemical tests of as-prepared Sn@C electrodes were performed with reference to Li+/Li at a current density of 200 mAh/g in the voltage range between 1.5 to 0.02 V. It yielded the high initial discharge capacity with the value of ~1220 mA h/g. The capacity delivered around 300 mAh/g even after 50 cycles. The carbon shell could accommodate the large volume change and prevent metal aggregation over repeated cycling. There are two main reasons for this performance: firstly, the imperfect active encapsulation of the Sn@C, may lead to agglomeration of the non-capsulated Sn particles and continuous formation of unstable SEI films on the surface of the electrode. Secondly, it could be resulted from very thin carbon layer (~10-20 nm) coated on the Sn surfaces. So, particles are pulverized which brings about swelling and capacity fading.





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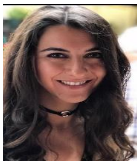

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In Situ Synthesis of Reduced Graphite Oxide-$Li_2ZnTi_3O_8$ Composite As a High Rate Anode Material for Lithium-ion Batteries

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In the present commercial LIBs, the graphite is a common anode material due to its low cost and rapid charge-discharge capability. However, a fatal problem for using this material is the dendritic lithium growth on the surface of the electrode during the overcharging process [1]. As a result, it is urgent to develop novel anode materials, which not only meet the increasing safety demand but also exhibit high energy density and good cycling stability. Cubic spinel $Li_2ZnTi_3O_8$ (LZTO) with a space group of $P4_332$ has exhibited good high discharge capacity and good cycle stability [2]. This material has a high discharge voltage plateau around 0.5 V which can inhibit the dendritic lithium growth over charge to 0 V. On the other hand, LZTO is able to accommodate Li^+ reversibly with a theoretical capacity of 229 mA h g^{-1} which is much higher than that of zero-strain $Li_4Ti_5O_{12}$ [3]. However, LZTO also suffers low electronic conductivity and ion diffusion rate. The poor electronic conductivity of LZTO still limits its rate capability and long-term cycling life.

In this study, we synthesized pristine LZTO and reduced graphite oxide modified LZTO (LZTO@RGO) samples via in situ ball mill assisted solid state method for the first time. RGO/LZTO mass ratios were selected as 0.1: 1, 0.25:1 and 0.5:1, respectively. The effects of RGO content on the crystal lattice, particle morphology and electrochemical properties were investigated.

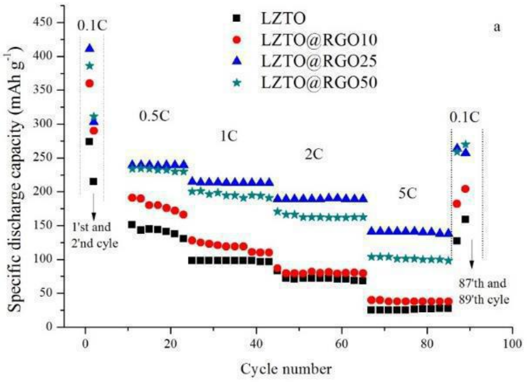

Figure 1. Rate capabilities of LZTO and LZTO@RGO anode materials

The specific capacity of LZTO@RGO anodes can be increased due to the fact that reduced graphite oxide layers can improve the lithium ion diffusion rate and the electronic conductivity. So, compared to pristine LZTO, RGO modified anodes have better electrochemical properties, such as specific capacity and high rate property.

The electrochemical performance of LZTO could be improved by adjusting the content of RGO. Among all the samples, LZTO@RGO25 exhibits excellent electrochemical performance in terms of high capacities (302, 250, 221, 194 and 154 mAh g^{-1} at current densities of 0.1, 0.5, 1, 2 and 5C, respectively).
As shown in Fig. 2, among all the samples, the LZTO@RGO25 anode has the highest discharge capacities at 0.1 C and 1 C rates, whereas the pristine LZTO anode has much less lithiation capacity under the same condition [4].

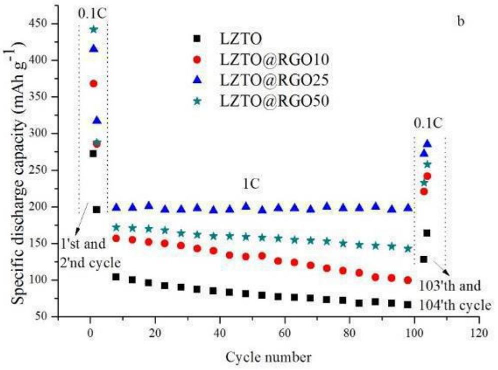

Figure 2. Cycling life performance of LZTO and LZTO@RGO anode materials at 1C current rate.

The enhanced electrochemical properties of the LZTO@RGO anodes may lead to potential applications for advanced lithium batteries.

Acknowledgements

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Current collector-free printed three-dimensional MXene-based anodes for lithium-ion batteries

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Lithium-ion batteries have risen to prominence as a cutting-edge and highly effective solution for energy storage systems. İt has attracted widespread applications spanning through various industries including; consumer electronics, electric transportation, biomedical devices, and renewable energy infrastructure. İn search to improve energy storagy systems, many researchers have turned to Mxenes as a highly promising option for anode materials. Mxenes which is optimized from MAXphase (Ti_3AlC_2) as shown in Fig.1 below belongs to a group of two-dimensional transition metal carbides and nitrides, have captured considerable interest due to their outstanding electrochemical properties and distinctive structural features.

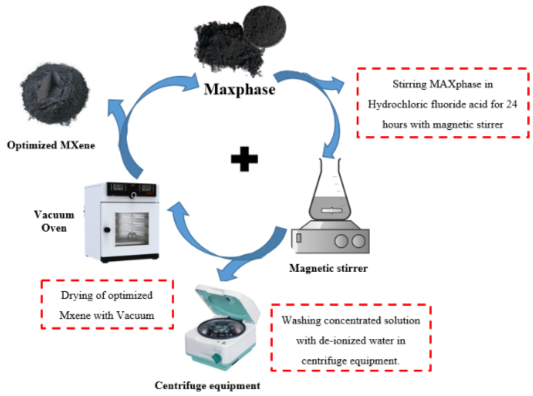

Figure 1. Optimization process of MAXphase to MXene.

As a printable anode material, the process was simple and scalable, which was achieved through 3D printing technique as shown in fig. 2 above.

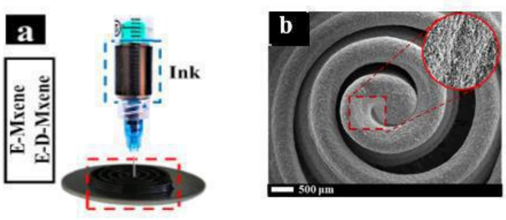

Figure 2. Illustration of 3D MXene ink printed electrodes with different layers

Technical characterization and electrochemical performance of the 3D MXene-based anodes was carefully analyzed including SEM, XRD, capacity, cycling stability, and rate capability, a specific capacity of 120 $mAhg^{-1}$ with almost 99.99% columbic efficiency after 100 cycles were obtained indicating that this approach has potentials to produce high performance batteries for the development and manufacturing of advanced next generation energy storage devices.

This paper aimed to reveal the dual functional properties of MXene as an active and conductive material for the development of lithium-ion batteries eliminating the need for additional current collector. Cost and weight reduction are the two advantages that this novel approach has promised during battery manufacturing.

Reference

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Improving electrochemical performances of sulfide-based solid battery by understanding and designing interface of cathode/electrolyte

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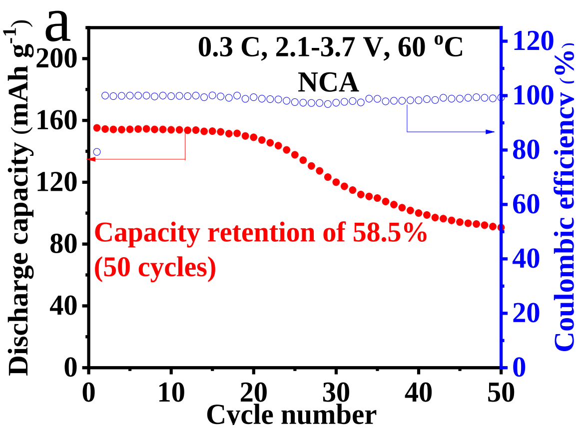
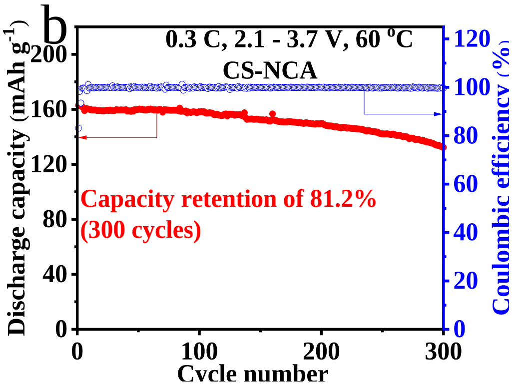
The interfacial instability between layered oxide cathode and sulfide electrolyte, especially for Ni-rich oxide cathode, is a serious issue for all-solid-state lithium batteries (ASSLB).[1] Coating with lithium ionic conductors such as LiNbO$_3$, Li$_2$SiO$_3$, Li$_4$Ti$_5$O$_{12}$ and Li$_2$O·ZrO$_2$ on the oxide materials is an effective method to reduce the interfacial impedance between oxide cathode and sulfide electrolyte. The coating material composition, morphology as well as covering degree of coating materials on surface of active cathode materials should play a important role on electrochemical performances of batteries. However, these investigations are seldom done in detail. In this work, the effect of crystallization degree of LiNbO$_3$ by controlling different sintering temperatures on the interface between LiCoO$_2$ and sulfide electrolyte is investigated. Moreover, the introduction of core-shell structure into Ni-rich NCA/NCM cathode materials can significantly improve the interfacial stability and thus increase the electrochemical performances of ASSLB with sulfide electrolyte, as shown in Fig.1. Ultimately, LiNbO$_3$-coated core-shell NCA/NCM can remarkably enhance the electrochemical performances of ASSLB.[2] In fact, the interfacial resistance between cathode and electrolyte indeed reduces gradually by introduction of core-shell structure and subsequent LiNbO$_3$-coating. The results indicate that the novel double bufer layers strategy is a more effective approach to design high-performance oxide cathode material for ASSLB using sulfide electrolyte. In addition, mechanical damage during cycling, severe interfacial side reactions and physical contact failure of cathode and solid electrolyte (SE) are investigated comparatively using single crystal NCM811 with different particle size as well as its polycrytal.





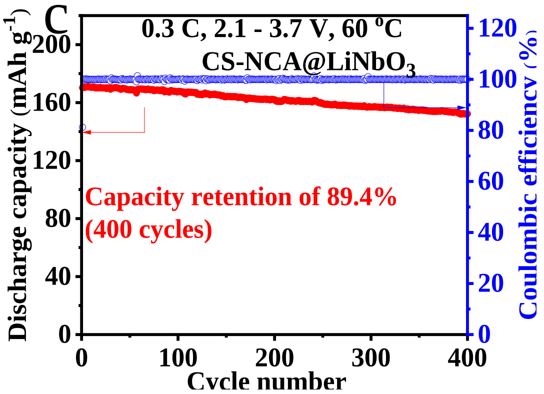


Figure 1. cycle performance curves of NCA, CS-NCA(core-shell structured NCA), and CS-NCA@LiNbO$_3$ (LiNbO$_3$ coated NCA woth core-shell structure) cathodes for ASSLB at 60 °C. 1 C=200 mA g-1.

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Prof Lianqi Zhang was born in 1973. He received his Ph d from Saga university in 2003 in Japan. After graduation he moved to national institute for materials science and work as a postdoctor with Prof. Takada in Tsukuba from April of 2003 to March of 2007. And then he continued his research still as a postdoctor in Tokyo institute of technology for one year. In 2008, he joined in Tianjin institute of power sources as a senior engineer In the end of 2010, he became professor in Tianjin university of technology. His research topics are forcused on inversitigations on cathode materials for Li ion battery, all solid state lithium battery as well as recycling spent Li ion battery.

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Coaxial Fiber-Shaped Highly Flexible Li-ion Battery for Powering Textile Electronics

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The stimulating desires of energy storage at millimeter scales for wearable technologies and IoT raise persistently, driving the advancement of integrable micro-power sources that can be comprehended due to pioneering researches in the chemistry of materials, battery architectures, and microfabrication developments. At this point, we propose an innovative strategy in the family of flexible coaxial fibrous Li-ion batteries by effectively implementing the unidirectional helical winding technique to accomplish multilayered tubules of all the cell components. In addition, the coaxial fiber battery encompasses an exclusively designed separator from a spunbonded polypropylene delivers auspicious electrochemical properties. Such a coaxial fibrous Li-ion batteries device presenting high energy storage capability is millimeter thin, highly flexible, and functions efficiently without compromising the total electrochemical performance of the battery. The full cell delivers a specific capacity of 137 µAh cm^{-1} at a 0.1C rate with almost 100% coulombic efficiency and is more capable of being functioned at several charging rates. The co-axial fiber battery was then altered well along to a spiral shaped flexible battery with outstanding stretchability.

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[3] M. Nasreldin, de Mulatier, S. R. Delattre, M. Ramuz, T. Djenizian, 5 (2020), 2000412.

Muniraj is currently a postdoctoral researcher at the Département d'Électronique Flexible of École des Mines de Saint Étienne, France. His post doc research focuses on the fabrication of flexible Li ion battery devices with various shapes and sizes using several electrode materials (cathode and anode). He received his Ph.D. in Chemical Sciences from CSIR National Chemical Laboratory, India, in October 2020. He is also a receipient of Raman Charpak Fellowship 2017 and visited the University of Lille, France. He has previously worked as post doctoral researcher in Pusan National University, Republic of Korea.

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Preparation of an ion-conductive LATP-based electrolyte thin film for lithum-ion microbatteries

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The progress in all-solid-state lithium-ion (Li^+) microbatteries, which is necessary for modern and future microelectronics, requires the development of high ionically conductive electrolytes. Among the various solid Li^+ electrolytes, the inorganic NASICON-type ceramic lithium aluminum titanium phosphate – $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP) has attracted high interest due to its air and water stability, high Li^+ conductivity and low cost. Though the ionic conductivity of crystalline bulk LATP is able to achieve ~10^{-3}–10^{-4} S/cm at room temperature (RT), the value for amorphous LATP film with thickness varies from 300 nm to 1000 nm currently does not exceed 10^{-6} S/cm and for crystalline 10^{-5} S/cm [1, 2, 3, 4].

Different techniques can be applied for synthesis of LATP thin films including sol-gel, magnetron sputtering (MS), pulsed laser deposition (PLD), spin-coating, aerosol deposition and etc. Among all methods, magnetron sputtering technique allows achieving thin films with smooth surface favorable for microbatteries due to its deposition feature. However, this synthesis method faces the problem of undesirable losses of lithium during sputtering and subsequent annealing.

Here we show that co-depositing of the film by two target sources, it is possible to reduce/compensate for the loss of lithium in the composition of LATP thin films during deposition. A series of depositions from LATP and Li_3PO_4 were carried out to study the effect of sputtering parameters, such as power (10-25%), deposition gas (Ar, N_2, O_2), on the composition and the ionic conductivity of the electrolyte film (Figure 1).

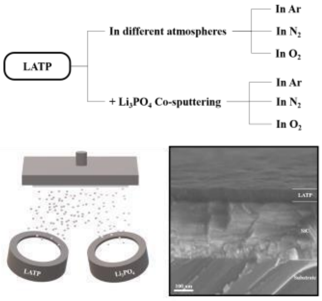

Figure 1. The schematically view of co-sputtering

Our results demonstrate how the deposition atmosphere affects the deposition rate and ionic conductivity of the thin films, as well as co-deposition with Li_3PO_4. In order to obtain the electrolyte films with the improved electrochemical characteristics, the parameters of the deposition process varied as well as the strategy to thin films' structure. Thus, the monolithic LATP sputtered in different gases, co-sputtered LATP and lithium phosphorus oxynitride (LiPON) with a general formula of $Li_xPO_yN_z$ were prepared and investigated. The film composition was determined by X-ray photoelectron spectroscopy (XPS) and inductively coupled plasma mass spectrometry (ICP-MS). A room-temperature conductivity σ_{RT} of ~10^{-6} S/cm is obtained for a thin LATP film obtained in nitrogen atmosphere. The compositional dependence of Li^+ transport mechanism is discussed.

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Synthesis of NiO Thin Film Electrodes via RF Magnetron Sputtering for In-Plane 3D Thin Film Batteries

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The use of transition metal oxides as anode materials for lithium-ion batteries (LIBs) has gained significant attention due to their high specific capacity compared to carbon-based materials. Among these oxides, NiO stands out for its affordability, ease of production, chemical stability, and high exciton binding energy. However, the low electrical conductivity and volume changes during the charge/discharge cycles limit the stability of NiO's specific capacity. To address these issues, thin-film electrodes synthesized using RF magnetron sputtering have been explored.

RF magnetron sputtering offers advantages such as the ability to produce large-area thin films suitable for industrial applications and the capability to sputter both conducting and non-conducting materials. The technique ensures the construction of dense structures and produces high-quality films with minimal contamination. The demand for LIBs has been rapidly increasing for portable electronic devices, electric vehicles, and energy storage applications. To achieve high energy density, increasing the electrode surface area is essential. Traditional planar electrode designs have limitations in terms of mass loading and thickness, which can be overcome by employing three-dimensional (3D) electrode configurations. 3D thin electrode structures allow for increased active material deposition while maintaining a smaller thickness, overcoming challenges associated with thick electrodes and volume variations during lithium-ion insertion and extraction.

Transition metal oxides, including NiO, have been investigated as replacements for graphite-based anodes due to their high specific capacities. However, they face challenges such as low cell voltage, poor charge transfer kinetics, and low initial coulombic efficiency. The low coulombic efficiency is primarily due to the formation of a solid electrolyte interphase (SEI) during the initial discharge process, as well as the volume expansion and fracture of the electrode material. To improve the initial coulombic efficiency of NiO electrodes, it is crucial to reduce the co-occurrence of the lithiation reaction and SEI formation.

This study focuses on the synthesis of NiO thin film electrodes using RF magnetron sputtering. The in-plane type 3D battery configuration, without the use of a commercial separator, demonstrates stable cycling ability with a capacity retention of 94% and a coulombic efficiency of 97% over 60 cycles. These results are promising for the development of in-plane type 3D thin film batteries, addressing the challenges associated with NiO-based electrodes.

Overall, the utilization of RF magnetron sputtering for NiO thin film electrodes in 3D battery configurations presents a potential solution to enhance the performance and stability of lithium-ion batteries. These findings contribute to the advancement of high-energy and high-power density battery systems required for various applications in the modern era.

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Development and Characterization of Perovskite Based Solid Electrolytes for Solid-State Lithium-Ion Batteries

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Liquid electrolytes cause safety problems used in lithium-ion batteries during overcharge-discharge and cause fires and explosions. This is due to the low operating temperature of liquid electrolytes (-15 to 60 °C) [1]. One solution to this problem is to switch from organic liquid electrolytes to solid electrolytes which have resistant to high temperatures. However, one of the most important obstacles to the use of solid electrolytes is their low ionic conductivity (on the order of 10^{-4} S/cm) [2]. The perovskit-oxide family which has ABO_3 structure draws attention due to its high ionic conductivity (10^{-3} S/cm), wide operation temperature (usually -40 to 150 °C). However, the ionic conductivity of the perovskite oxide family is not as high as the liquid electrolyte conductivity (10^{-2} S/cm), which limits their usage for practical applications. That is why there are studies focusing to enhance the ionic conductivity of perovskite oxides. One of the most important strategies is that doping A-site with an element having large ionic radius. The reason is that it causes an increase in ionic conductivity with expansion of octahedral channels in the A-site where Li ions are transported [3].

In this study, $Li_{1-x}M_xFeO_3$,(x=0,1, 0,3, 0,5, 0,7, 0,9) (M=Sr, Ba, Ce (r=1.44, 1.61, 1.34 Å)) were selected which was synthesized by Pechini method. It was aimed to observe effect of A-site doping and have higher ionic conductivity (>10^{-3} S/cm). LCFe371, LBFe371, and LSFe371 perovskites were synthesized with/without pH control to obtain perovskites without an impurity. The produced perovskites have been subjected to calcination at 900 °C for 6 hrs. X-ray diffraction (XRD) was performed to determine the crystal structure of perovskite materials synthesized. XRD patterns were collected with a scan rate of 2°/min as shown in Figure 1.

In conclusion, under the same experimental conditions, it was observed that the addition of Sr resulted in the formation of a cubic structure in the synthesized perovskites, while the addition of Ba led to the formation of a hexagonal structure. In both structures, $LiFeO_2$ was formed as a secondary phase. In the case of the Ce-doped structure, the formation of a perovskite structure was not observed. When the pH was adjusted to 7.5 for all three compositions, although there was a slight increase in material purity, the overall results remained the same (Figure 1).

To overcome this issue, in the next step, the calcination temperature will be increased to 1000 °C for the analysis.

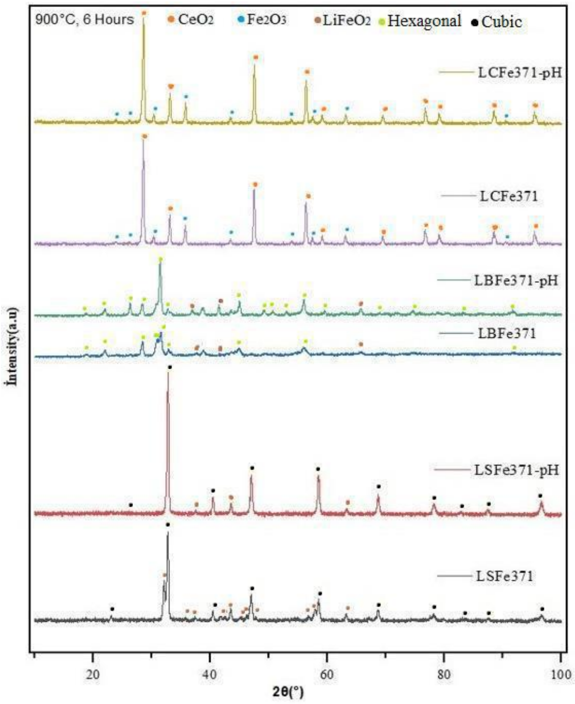

Figure 1. XRD model of pH comparison of LSF, LBF, LCF.

After obtaining the perovskite materials in their pure form, impedance spectroscopy (EIS) will be employed to measure the ionic conductivity of the samples.

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The mixed ionic and electronic conductor LLZO solid electrolytes for lithium-ion battery cathodes

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Ni-rich layered oxide cathode materials for Li-ion batteries decompose by reacting with the liquid electrolyte species, and their capacity is reduced during cyclic charge and discharge. Therefore, the cathode surface is coated to prevent reactions between the liquid electrolyte and the cathode material. $Li_7La_3Zr_2O_{12}$ (LLZO) is a potential candidate as a coating material due to its high ionic conductivity and chemical stability [1]. When the cathode surface is coated with LLZO, a protective interface is formed between the cathode material and the liquid electrolyte. Therefore, the cathode active material surface is protected from unwanted side reactions without compromising the Li-ion transport. Thus, the surface of the active cathode material becomes more stable, its cyclic stability is improved, and the battery life is extended [2]. On the other hand, solid electrolyte materials with good Li ion conductivity are poor in electronic conductivity. The slowdown in electron transport between the cathode and the current collector adversely affects the rate performance of the battery. Therefore, the electronic conductivity of LLZO solid electrolyte coatings for cathode surface modification must be improved. Substitution of elements such as Fe, Ni, and Co into the LLZO is known to improve electron transport as well as Li-ion transport. Cheng et al. synthesized the garnet-type LLZO by introducing Fe, Co, and Ni, improving its electronic conductivity around 2.75×10^{-6} S cm^{-1} by Co doping [3]. Samson et al. reported the effect of Mn, Fe and Co doping on the cubic structure of garnet-type cubic $Li_7La_{2.75}Ca_{0.25}Zr_{1.75}Nb_{0.25}O_{12}$ structure. Among these elements, 0.1 Co doping provided a good combination of ionic conductivity (2.5×10^{-4} S cm^{-1}) and electronic conductivity (10^{-8} S cm^{-1}) [4].

In this study, garnet-type cubic LLZO was synthesized by doping Ni, Co, and Urea to improve its electronic conductivity. Composite electrodes were prepared by homogeneously mixing the synthesized LLZO and the active particles of the commercial NMC622 cathode. The crystal structure of the NMC622/LLZO compounds is shown in Figure 1. It can be seen that the cubic-LLZO is formed, and the layered structure of NMC622 is maintained. Galvanostatic charge/discharge tests were carried out to see the effect of the LLZO dopant on the battery performance. Li-ion cells having NMC622/LLZO composite cathode using Ni, Co and Urea as a dopant have improved discharge capacity at 1C rate than the undoped sample (Figure 2). All in all, the enhanced rate performance of the composite cathodes having doped LLZO solid electrolytes is attributed to the enhanced electronic conductivity.

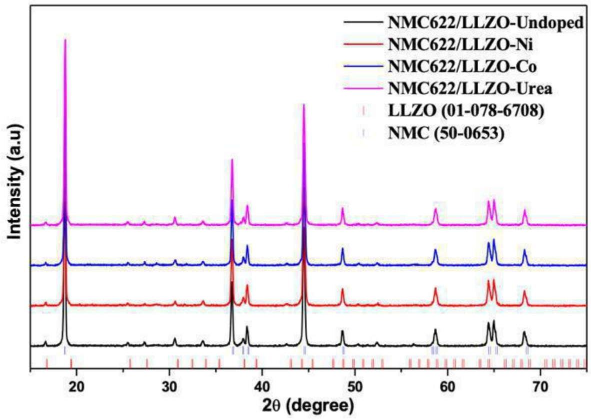

Figure 1: XRD analysis of the NMC622/LLZO-X doped (X=Ni,Co and Urea) composite electrodes

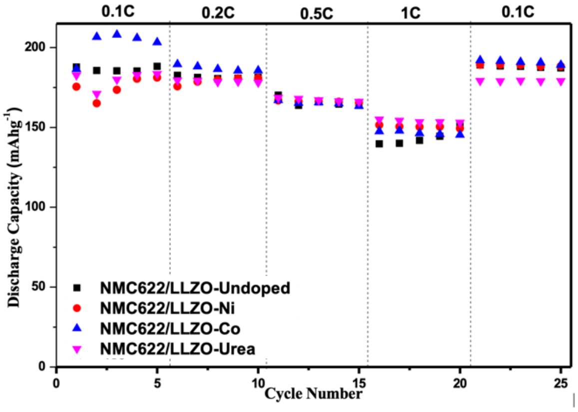

Figure 2: Rate performance of the NMC622/LLZO-X doped (X=Ni,Co and Urea) composite electrodes between 2.75V and 4.6 V versus Li$^+$/Li.

Acknowledgements

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Investigation of the Mechanisms of Polaron Conduction in Cathode Materials of Na and K-Ion Batteries.

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Due to increasing demand in stationary and portable energy storage an extensive research of new electrode materials for metal-ion batteries is performed nowadays. In contrast to Li-ion, sodium ion and potassium ion batteries are cheaper and allows to mitigate the risks associated with lithium production concentrated in a few countries, while Na is one of the most abundant elements on Earth. However, sodium-based materials are suffering from poor electronic conductivity such as in the case of hexacyanoferrate (HCF) based cathode, e.g. $Na_2Fe_2(CN)_6$ [1]. The electronic transport in HCF and other insulating cathode materials proceeds by the polaron hopping mechanism calling for its thorough investigation as it has a strong impact on a battery rate performance.

According to experimental results the rate performance of $KTiOPO_4$-type based (KTP) cathode materials ($NaVPO_4F$, $KVPO_4F$, $KTiPO_4F$) is several orders of magnitude higher than that of hexacyanoferrate based (HCF) materials ($Na_2Fe_2(CN)_6$) [2, 3]. However, it remains unclear what are the physical reasons for the observed differences between these two classes of materials. There is a hypothesis that it originates from the different transport of small polaronas. Unfortunately, little is known about the small polaron behavior in either of the two classes of materials. Therefore, in this study we perform a computational study of small polaron transport using Density Functional Theory (DFT) by calculating polaron migration barriers and polaron formation energies.

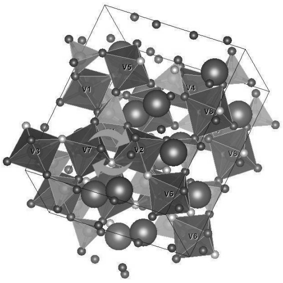

Figure 1. KTP-type structure and directions of investigated polaron hoppings.

All materials are modeled using generalized gradient approximation (GGA) with Hubbard correction and standard PAW PBE potentials as implemented in VASP software. To form an electron (hole) small polaron we add (remove) one electron and slightly distort a required octahedron by adjusting M-O, F distances. To calculate migration path we use a linear interpolation scheme $q(x) = xq_A + (1 - x)q_B$, where $0 < x < 1$, q_A — structure with polaron on initial site, q_B - with polaron on final site. We investigate migration barriers of hole polarons for intercalated structures ($NaVPO_4F$, $KVPO_4F$, $KTiPO_4F$) and electron polarons for deintercaleted structures (VPO4F, TiPO4F).

By comparing several compounds with the same crystal structure but different chemical composition we rationalized the impact of alkali and transition metal elements on the formation and migration energies of polarons. For non-equivalent TM sites the polaron formation energies can differ by up to 0.25 eV causing an additional increase of migration barriers. The polaron localization is more preferable for more symmetric octahedra, while fluorine displacement has strong impact on polaron formation. The calculated migration barriers suggest that the electronic conductivity should decrease in the following order: $KVPO_4F$ > $NaVPO_4F$ > VPO_4F > $KTiPO_4F$ > $TiPO_4F$, respectively. The smallest barrier of 0.18 eV was obtained for $KVPO_4F$, which is smaller than that in commercially produced $LiFePO_4$ [4]. The preliminary results confirm the proposed hypothesis that the polaron migration barriers in KTP are smaller than that in HCF materials. This results explains the origin of high performance of KTP materials and provide a rationale for their further optimization.

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Matching Electrochemical Properties and Phase Transformations in NASICON-type Electrode Materials for Na-ion batteries

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NASICON-type $Na_3V_2(PO_4)_3$ cathode materials are considered as promising candidates for high-performance Na-ion batteries due to extremely long cyclic stability and an outstanding ability to operate at high (dis)charge rates. However, its cost-effectiveness can still be improved using transition metals cheaper than vanadium, which could also increase the energy density compared to that in $Na_3V_2(PO_4)_3$.

The replacement of V with Mn and Cr in $Na_3V_2(PO_4)_3$ lowers the cost of the materials and enhances the operation voltage. Substitution of V by electrochemically inactive Mg and Sc allows studying vanadium redox processes without contributions from these metals (Figure 1).

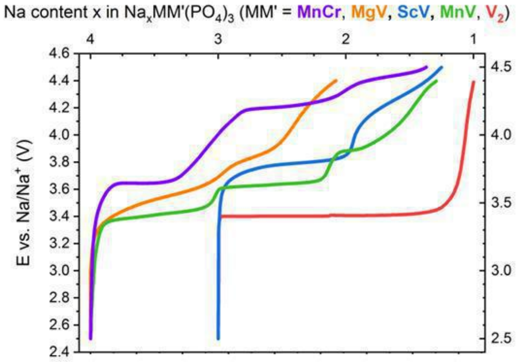

Figure 1 Comparison of galvanostatic charge curves of NASICON compounds with different composition.

When the voltage window above 3.8 V is utilized, Mn^{2+} substitution enhances the energy density of $Na_{3+x}Mn_xV_{2-x}(PO_4)_3$ compounds for up to 10% compared with the $Na_3V_2(PO_4)_3$. The evolution of the transition metal oxidation states in $Na_4MnV(PO_4)_3$ during charge and discharge was studied by X-ray absorption spectroscopy (XAS) in *ex situ* and *operando* regimes using an electrochemical cell with X-ray transparent windows.

In order to link electrochemical features with the phase transformations in NASICON samples *operando* X-ray powder diffraction was carried out (Figure 2). The crystal structure changes on charge and discharge were studied as well as the electrode performance in narrow (2.5-3.8 V), wide (2.5-4.5 V) and extra wide (1.0-4.5 V) potential windows.

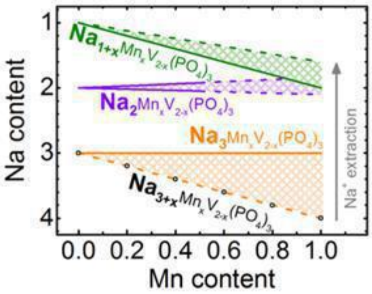

Figure 2 Schematic illustration of the Na^+ deintercalation regimes from $Na_{3+x}Mn_xV_{2-x}(PO_4)_3$ ($0 \leq x \leq 1$).

The results indicate that in case of narrow voltage window the Na^+ (de)intercalation reaction is reversible, however for the V-substituted compounds charging above 3.8 V increases energy density, but leads to the loss of reversibility and capacity fade. However, for some compounds an overdischarge below 2.5 V suppresses the capacity fade [1].

The experimental results indicate the benefits of vanadium-substituted compounds and ability to outperform the unsubstituted materials in terms of rate-capability. Therefore they should be preferred for high-power applications.

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Novel vanadium-based phosphates as sodium-ion battery positive electrodes

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The realization and commercialization of sodium-ion batteries vastly relies on the advances in positive electrode materials having superior electrochemical properties [1]. Among the existing materials, there is a competition between oxide and polyanion families: while the former averagely display higher capacities and energy density, the latter show unprecedented long-cycling stability and power characteristics. Moreover the polyanion materials possess a rich variety of structural types that provides a huge playground for designing new materials with unique properties.

In this work, we offer a new class of positive electrode materials designed by merging a promising $NaVPO_4X$ (X = F, O) chemical composition and a high-rate $KTiOPO_4$-(KTP)-type structural framework with promising transport properties. This fusion is enabled by a devised low-temperature synthesis approach composing of two stages: hydrothermal treatment and chemical ion-exchange reaction. Being superior to most of the renowned Na-based cathodes, these electrode materials exhibits steady high-voltage and high-power electrochemical performance. Depending on the X the materials deliver up to 130-135 mAh g^{-1} of reversible capacity (more than 90% of the theoretical values, Figure 1) at a C/10 rate at average discharge potentials of 3.7-4.0 V vs. Na^+/Na (depending on the X). At higher rate of 10C the materials show up to 100 mAh g^{-1} (with high loading of 22 mg cm^{-2} of active material, equal to 3 mAh cm^{-2}). The de/intercalation and charge compensation mechanisms of the materials were studied by operando and ex situ XRD and XAS techniques. The fluoride phosphate representative follows mostly an advantageous solid-solution mechanism, whereas turning to oxophosphate brings about several minor phase transitions possibly associated with charge ordering in the lattice. From a practical point of view, the materials validate their commercial elegibility in steady-functioning 4 V hard carbon-anode-based full cells. Overall, KTP-type $NaVPO_4X$ phosphates unravel the practical specific energy of in the range of 480-540 Wh kg^{-1} setting a new standard for the polyanion Na-ion battery positive electrodes.

In the presentation, different aspects of synthesis, crystal structure refinement, materials characterization and electrochemical properties of these new KTP-type phosphate cathode materials will be presented with particular attention to the composition-structure-property relationships; as well as de/intercalation and charge compensation mechanisms studied by ex situ and operando XRD/XAS. A special emphasis will also be given to the place of KTP-$NaVPO_4X$ among the multitude of polymorphs and closely-related cathode materials.

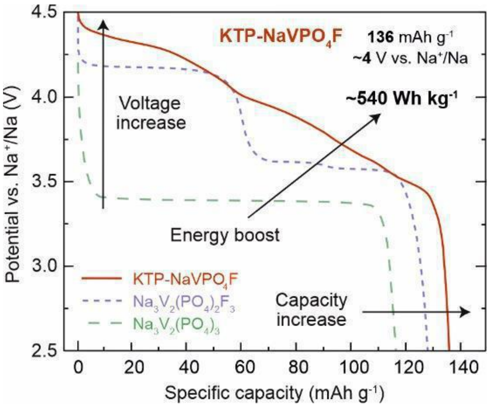

Figure 1. Potential vs. specific capacity plots for $Na_3V_2(PO_4)_3$, $Na_3V_2(PO_4)_2F_3$, normalized to the theoretical specific capacity per one-electron V^{3+}↔V^{4+} transition. For KTP-$NaVPO_4F$, the experimental discharge profile is presented for comparison..

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Role of Ni and Fe redox activity in electrochemical properties of O3-NaFe1-x-yNixMnyO2 materials as cathodes for Na-ion batteries

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Na-ion batteries are considered as future alternative to Li-ion due to low cost and wide abundance of sodium. In turn, O3-type $NaNi_{1-x-y}Fe_xMn_yO_2$ cathode materials are an excellent alternative to Li-containing layered oxides such as $LiCoO_2$ and its derivatives [1]. These compounds are isostructural to α-$NaFeO_2$ (s.g. $R\bar{3}m$) with Ni, Fe, and Mn in $NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_2$ being in the 2+, 3+, and 4+ oxidation states, respectively. The possibility of using Fe^{3+}/Fe^{4+} redox pair in cathode materials for SIBs is one of the main features of the Na-ion system in contrast to Li-ion. However, the peculiar crystal chemistry of iron cations introduces certain problems in the (de)sodiation process of layered sodium oxides. Its stable electrochemical performance is restricted by the upper voltage limit of 4.0 V (vs. Na/Na^+), which allows for reversibly removing 0.5-0.55 Na^+ per formula unit, corresponding to the capacity of 120-130 $mAh\cdot g^{-1}$. Further reduction of sodium content inevitably accelerates capacity degradation, and this issue calls for a detailed study of the redox reactions that accompany the electrochemical (de)intercalation of a large amount of sodium.

Here, we present operando and ex situ studies using powder X-ray diffraction (PXRD) and X-ray absorption spectroscopy (XAS) combined with ^{57}Fe Mössbauer spectroscopy (MS). Our approach reveals the sequence of the redox transitions that occur during the charge and discharge of O3-$NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_2$. A combination of operando XAS and MS experiments revealed that Ni is the only electrochemically active d-cation at the beginning of charge up to x≈0.25 in $Na_{1-x}Ni_{1/3}Fe_{1/3}Mn_{1/3}O_2$. Further (de)sodiation includes oxidation of both Fe^{3+} and Ni^{3+}. In addition to nickel and iron cations oxidizing to M^{4+}, a part of iron transforms into the "3+δ" state owing to the fast electron exchange $Fe^{3+} + Fe^{4+} \leftrightarrow Fe^{4+} + Fe^{3+}$. This process freezes upon cooling the material to 35 K, producing Fe^{4+} cations, some of which occupy tetrahedral positions. Our results are depicted in Figure 1 as a schematic representation of the redox transitions [2].

To study the influence of Fe and Ni redox activity in more depth, we synthesized O3-$NaNi_{1-x-y}Fe_xMn_yO_2$ (111NFM, 121NFM, 112NFM and 211NFM) materials and performed their electrochemical studies (Figure 2). On the one hand, increasing of Fe content in O3- $NaNi_{1-x-y}Fe_xMn_yO_2$ material accelerates capacity degradation, on the other hand high content of Fe increases the average discharge potential of material.

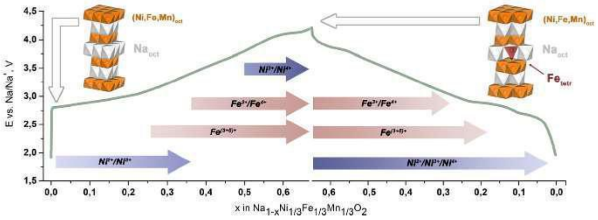

Figure 1. Redox transformations of Fe and Ni cations in O3-$Na_{1-x}Ni_{1/3}Fe_{1/3}Mn_{1/3}O_2$ during charge/discharge.

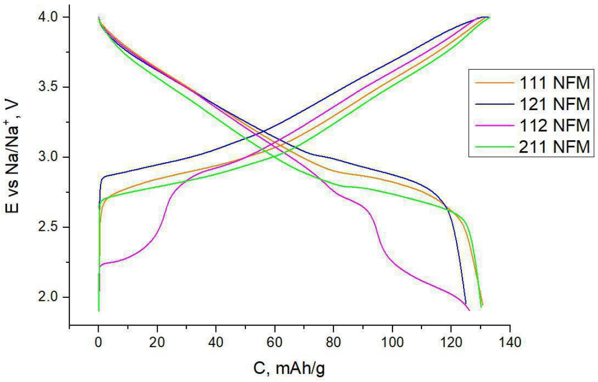

Figure 2. Charge-discharge curves of O3-type $NaNi_{1-x-y}Fe_xMn_yO_2$ cathode materials.

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Effect of molar ratios of Ni, Mn, and Fe on structural stability and electrochemical performance of layered cathode materials for sodium-ion batteries

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The increasing adoption of renewable energy necessitates the increase in the development of efficient and affordable energy storage technologies. Since intermittent renewable energy sources such as wave, solar, and wind need to turn into dominant and integrated into the power grid, there is a demand for large-scale energy storage solutions [1]. Modern market is dominated by lithium-ion batteries. The dominance of LIBs can be attributed to low self-discharge rates, high coulombic efficiency, high energy density, and a spectrum of chemical potentials available with various electrode designs [2]. Even though LIB technology is well-established, there are still issues regarding its cost-effectiveness, lifetime, safety, and performance at low temperatures [2]. Additionally, since there is high demand for lithium, which is not considered abundant in the Earth's crust, its feasibility for large-scale utilization has begun being questioned. Ongoing research on cathode materials is aiming to replace the most expensive and important part with more affordable and superior replacement. Sodium-ion batteries (SIBs) have a slight disadvantage over LIBs such as low electrochemical potential of -2.71 V compared to the standard hydrogen electrode (SHE) which is only slightly higher than that of LIBs (330 mV), However much more abundant, thus enabling SIBs meet requirements of large-scale electrical energy storage [1]. Polyanionic compounds, layered oxides, Prussian blue analogs, and organic compounds are the materials that have been extensively investigated as potential positive electrodes for SIBs. Layered transition metal oxides (TMO) are a type of cathode material with greater capabilities regarding up-scalability, energy density and stability [3]. Among TMOs $NaMnO_2$ based cathode materials are competitive as low-cost and high-power cathode material. However, the complex phase transitions with large volume changes during cycling leads to rapid degradation of the crystal structure and as a result capacity. Recent investigation suggests that undesirable phase transformation can be dampened via doping additional transitional TMs into the structure [3].

O3-$NaNi_{0.5}Mn_{0.5}O_2$ transition metal oxide, as reported by Komaba et al., is one of the most promising cathode materials for SIBs because of its good cycling performance with capacity retention of 81% after 20 cycles and capacity of 120 mAh g^{-1} [4]. Following this, they substituted $Ni_{0.5}Mn_{0.5}$ with Fe in O3-NaFeO2 to create O3-$Na(Ni_{0.5}Mn_{0.5})_{1-x}Fe_xO_2$ and proposed $NaNi_{1/3}Mn_{1/3}Fe_{1/3}$ as the optimum material due to a balance between capacity, cycling, and cost [5]. Currently, the full extent of effects of different concentrations of Fe and Ni as well as of Na on electrochemical performance and structural changes of NaNiFeMnO have not been fully studied.

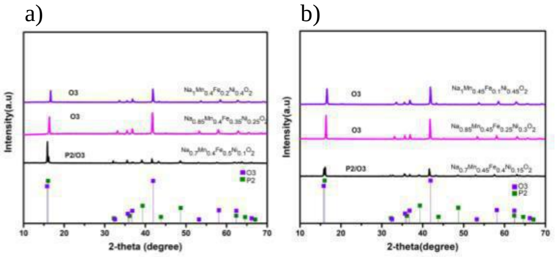

Figure 1. a) XRD data for $Na_xMn_{0.4}Fe_yNi_{0.6-y}$ cathode materials. b) XRD data for $Na_xMn_{0.45}Fe_yNi_{0.55-y}$ cathode materials.

In this research, we studied the combination of different ratios of Ni, Mn, and Fe in O3 and P2 type $NaNi_xMn_yFe_{1-(x+y)}O_2$ cathode material. $NaNi_xMn_yFe_{1-(x+y)}$O2 has been synthesized via solid-state method in open air. During experiments, the correlation between the characteristics of the material (both morphological and electrochemical) and concentrations of the elements has been investigated. $Na_{0.7}Mn_{0.4}Fe_{0.5}Ni_{0.1}O_2$ and $Na_{0.7}Mn_{0.45}Fe_{0.4}Ni_{0.15}O_2$ cathode materials exhibited biphasic P2/O3 structure while $Na_{0.85}Mn_{0.4}Fe_{0.35}Ni_{0.25}O_2$ and $Na_{0.85}Mn_{0.45}Fe_{0.25}Ni_{0.3}O_2$, $Na_{0.95}Mn_{0.4}Fe_{0.25}Ni_{0.35}O_2$ and $Na_{0.95}Mn_{0.45}Fe_{0.15}Ni_{0.4}O_2$, $Na_1Mn_{0.4}Fe_{0.2}Ni_{0.4}O_2$ and $Na_1Mn_{0.45}Fe_{0.1}Ni_{0.45}$ corresponded to O3 structure. Further XPS, SEM-EDS, ICP-OES, and electrochemical studies were done to investigate the link between the structure and electrochemical performance.

Acknowledgements

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Effect of Fe-subtitution on electrochemical performance of Mn-based Prussian blue as cathode material for sodium ion batteries

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Sodium-ion batteries (SIBs) based on cost-effective and naturally abundant sodium cation have become potential candidates for low cost and sustainable EESs [1]. The cathode active materials plays a key role in overall performance of SIBs. Among the cathode active materials, Prussian blue (PB) and its analogues (PBAs) have been considered as one of the most promising cathode materials for sodium ion batteries because of low material cost, facile synthesis and ecofriendliness. However, Jahn-Teller effect of Mn^{3+}, phase transitions and Mn^{2+} dissolution could induce the structural variation of sodium manganese hexacyanoferrates (MnHCFs), leading to low cycling stability, low Coulombic efficiency and low specific capacity. In order to improve structural stability water resistant and conductivity and suppress the phase transitions of Na-layered metal oxides over a wide compositional range, some methods such as elemental doping, morphology engineering, compositing with conductive materials and crystallization control have been demonstrated to be an efficient method. Aiming to address these issues, herein, Fe^{2+} substitution for Mn^{2+} is carried out to obtain $Na_{1.34}Mn_{0.50}Fe_{0.50}[Fe(CN)_6]_{1.00}.2.09H_2O$ cathode material. The sharpe peaks in the XRD pattern (Fig.1) of $Na_{1.34}Mn_{0.50}Fe_{0.50}[Fe(CN)_6]_{1.00}.2.09H_2O$ show that the crystal property of $Na_{1.34}Mn_{0.50}Fe_{0.50}[Fe(CN)_6]_{1.00}.2.09H_2O$ is better than that of $Na_{1.77}Mn[Fe(CN)_6]_{1.05}.1.34H_2O$. The conductivities of $Na_{1.77}Mn[Fe(CN)_6]_{1.05}.1.34H_2O$ and $Na_{1.34}Mn_{0.50}Fe_{0.50}[Fe(CN)_6]_{1.00}.2.09H_2O$ cathode materials were found to be $1.8x10^{-8}$ and $3.8x10^{-7}$ $S.cm^{-1}$, respectively. When these materials coupled with with hard carbon (HC) anode, the full cells $HC/Na_{1.77}Mn[Fe(CN)_6]_{1.05}.1.34H_2O$ and $HC/Na_{1.34}Mn_{0.50}Fe_{0.50}[Fe(CN)_6]_{1.00}.2.09H_2O$ can show the energy density of 161 and 197 Wh kg^{-1} at 0.1C (1C=170 mAh/g) at an average voltage of 3.3 V, respectively, based on the total mass of cathode and anode materials. The full cells, $HC/Na_{1.77}Mn[Fe(CN)_6]_{1.05}.1.34H_2O$ and $HC/Na_{1.34}Mn_{0.50}Fe_{0.50}[Fe(CN)_6]_{1.00}.2.09H_2O$ can give the energy densities of 106 and 117 Wh kg^{-1} after 50 charge/discharge cycles at 0.5C, indicating that Fe^{2+} substitution for Mn^{2+} can improve the electrochemical performance of MnHCFs due to increases of its structural stability and conductivity. These desired performances of $Na_{1.34}Mn_{0.50}Fe_{0.50}[Fe(CN)_6]_{1.00}.2.09H_2O$ make it a promising cathode material for practical applications in SIBs.

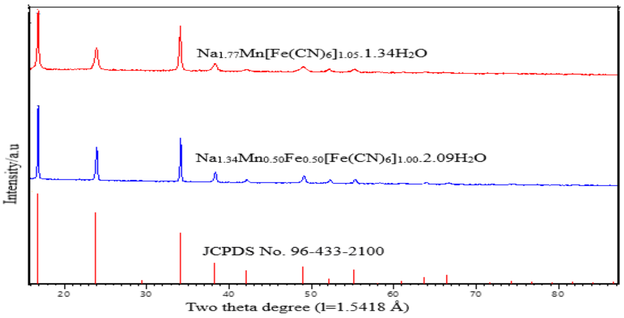

Figure 1. Powder XRD patterns of the **a)**$Na_{1.77}Mn[Fe(CN)_6]_{1.05}.1.34H_2O$ and **b)**$Na_{1.34}Mn_{0.50}Fe_{0.50}[Fe(CN)_6]_{1.00}.2.09H_2O$ samples

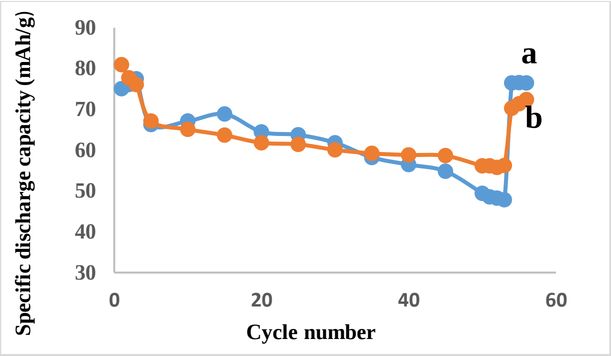

Figure 2. Cycling performance of the **a)**HC/0.5M $NaPF_6$ and 0.1M $NaBF_4$ in EC-DEC (1:1)/$Na_{1.77}Mn[Fe(CN)_6]_{1.05}.1.34H_2O$ and **b)**HC/0.5M $NaPF_6$ and 0.1M $NaBF_4$ in EC-DEC (1:1)/$Na_{1.34}Mn_{0.50}Fe_{0.50}[Fe(CN)_6]_{1.00}.2.09H_2O$ in the voltage range of 2.0−4.0 V at the current density of 85 mA g^{-1} (1C=170 mAh/g)

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Co-precipitation synthesis of spherical chromium-based layered oxide cathodes for sodium-ion batteries

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Nowadays, sodium-ion batteries (SIBs) are receiving increased attention from researchers, since they are considered as a low-cost complement to lithium-ion batteries: unlike lithium, sodium is abundant in the Earth's crust and evenly distributed geographically. Therefore, SIBs are a possible alternative technology for large-scale application, such as electric vehicles and grid energy storage. The main concern in their development is finding the appropriate electrode materials, especially cathode materials, which primarily determine the energy density of the battery. The majority of cathode materials for SIBs under investigation are polyanionic compounds, metal oxides, hexacyanometallates and organic compounds. Among them, transition metal oxides Na_xMO_2 with layered structure are considered as one of the most promising candidates, since they have high reversible capacity and operation potential, are easy to synthesize, and can be modified to achieve the desired properties, since unlike analogous Li-based oxides, almost all Na_xMO_2 compounds are able to reversibly intercalate Na^+ ions [1].

To fully take advantage of the low cost and environmental friendliness of SIB technology, the use of scarce or expensive metals in the cathode material should be reduced. To solve this problem, chromium-based layered oxides were applied as cathodes for SIBs, with O3-$NaCrO_2$ being the most widely investigated material, which showed relatively high average voltage and good energy density [2]. However, another challenge in the design of cathode materials is increase of their tap density using morphology modification. A promising approach towards layered oxides with high tap density is the use of co-precipitation step in the synthesis of hydroxide precursors, which provides spherically agregated uniform particles [3]. In this work, this approach is applied to chromium-based cathode materials. Coating and doping strategies are applied in order to achieve a material with desired properties, including high voltage and capacity, stability and conductivity.

In the poster, synthesis condition of chromium-based layered oxides will be discussed as well as the different types of carbon coatings.

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Key aspects for the development of hard carbon anode materials with advanced performance in sodium-ion batteries

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Hard carbon (HC) is the most promising and scalable anode material for sodium-ion batteries (SIBs). HC do not cost much and can be synthesized using carbon-based precursors such as saccharides, phenolic resins, and biomass [1-3]. HC demonstrate superior characteristics compared to all other carbonaceous materials for SIBs as sodium ions cannot be intercalated into graphite structure in a significant amount [4]. However, the initial Coulombic efficiency (ICE) and the discharge capacity is still lower compared with graphite anodes in lithium-ion batteries. Thus, it is of great importance to produce HCs with electrochemical characteristics. Moreover, the mechanism of sodium ion intercalation is still debatable and should be thoroughly investigated.

In this work, we consider many sources of hard carbons as carbohydrates, biopolymers and biomass. Pretreatment methodics of precursors as air pretreatment including caramelization of carbohydrates, hydrothermal carbonization and template synthesis were also consedered. Obtained intermediates and HCs were investigated using FTIR-spectroscopy, elemental analysis, small angle and wide angle X-Ray scattering (SAXS/WAXS), BET surface area measurements, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and scanning transmission electron microscopy (STEM) with integrated differential phase contrast (DPC). The electrochemical performance of half and full cells was tested by galvanostatic charge-discharge cycling.

We have demonstrated the importance of the accurate choice of conditions of the pretreatment stage for the synthesis of hard carbon anode material. Tuning the temperature and the regime of caramelization or hydrothermal carbonization as the first stage of synthesis could help to produce hard carbon with different morphological features, such as the “monolithic” carbon and microsperic morpholigy with close-to-zero surface. Obtained HCs demonstrated excellent ICE up to 91% with a capacity over 300 mAh g^{-1} in a sodium half-cell configuration. Furthermore, the correlation between the electrochemical performance, the morphology, the surface area, defectiveness, the surface atomic ratio of C:O was established.

Additionally, for the first time, hard carbons were obtained from Heracleum sosnowskyi, a highly invasive plant, which is dangerous for humans and can cause skin burns but produces a large amount of green biomass in a short time. We proposed a simple synthesis method that includes the pretreatment stage and further carbonization at 1300 °C. Obtained materials demonstrate >220 mAh g^{-1} of the discharge capacity, high values of the initial Coulombic efficiency reaching 87% and capacity retention of 95% after 100 charge-discharge cycles in sodium half-cells.

The sodium-ion storage mechanism was also studied. Based on *operando* Raman spectroscopy, *operando* X-Ray diffraction, *ex situ* STEM/DPC, *ex situ* SAXS/WAXS, we proposed the combination of adsorption process, intercalation and pores filling at different stages of the sodiation/desodiation.

Acknowledgements

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The synthesis of hard carbon anode material for sodium-ion batteries via hydrothermal carbonization.

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The need for energy storage systems is growing every year, sodium-ion batteries (SIBs) can be used as such sources, which are a promising alternative to lithium-ion batteries (LIBs). The key problem in the commercialization of the technology is the search for electrode materials with satisfactory electrochemical characteristics. Graphite, an anode material in lithium-ion batteries, is not suitable for SIBs, since sodium ions do not intercalate into the interlayer space of graphite. For SIBs anodes, non-graphitizable hard carbon materials are used, the structure of which contains disordered graphene-like layers.

Hydrothermal carbonization followed by high-temperature annealing can be used for the synthesis of hard carbon anode materials. It allows to obtain hard carbon with small particle size (~ 1µm) and low specific surface area (~1 m2), which should have a positive effect on the electrochemical characteristics of the material. Also, one of the features is the possibility of varying the synthesis parameters over a wide range. But the influence of the parameters of hydrothermal synthesis on the electrochemical characteristics of hard carbon remains an open question. The aim of this work is to develop synthetic approaches based on hydrothermal carbonization to obtain hard carbon with improved electrochemical characteristics.

Glucose was chosen as the carbon source. To achieve this goal, we investigated how the parameters of hydrothermal carbonization can affect the properties of hard carbon. For this, the concentration of glucose solution, temperature, and duration of hydrothermal carbonization were varied. The second stage of synthesis was high-temperature annealing in an inert atmosphere at 1300°C. The obtained samples were analyzed using various methods: FTIR spectroscopy, elemental CHNOS analysis, low temperature nitrogen adsorption, scanning electron spectroscopy, and galvanostatic cycling.

Hard carbon obtained by hydrothermal carbonization demonstrates high ICE up to 91% and good reversible capacity ~300 mAh/g. SIB's prototypes based on hard carbon and $Na_3V_2(PO_4)_2O_2F$ and $Na_3V_2(PO_4)_3$ cathode materials demonstrate good electrochemical characteristics: an ICE of about 80% and a discharge capacity of about 100 mAh/g, as well as good cycling stability (capacity retention of 90% for 100 cycles).

It was shown, that the morphology of hard carbon, namely, the particle size, on which the specific surface area depends, has a significant effect on ICE. A high concentrationa of glucose and low pH allows to obtain material with desired particle size and reduced the surface area. A temperature of 200°C and a duration of 3 hours is sufficient for hydrothermal carbonization to occur, and a further increase in these values does not lead to an improvement in the properties of the material. The obtained samples of hard carbon have suitable characteristics for successful application in sodium-ion batteries.

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Origins of irreversible capacity loss in hard carbon negative electrodes for potassium-ion batteries

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Hard carbon (HC) is a well-known negative electrode material for potassium-ion batteries, but it suffers from significant irreversible capacity loss at the first discharge cycle. We studied possible reasons of this capacity loss targeting the electrode/electrolyte interphase formation process in carbonate-based electrolyte with and without vinylene carbonate (VC) as an additive.

The studied HC consists of curved graphitic layers arranged into short packets and round cages, the latter acting as traps for K+-ions causing low Coulombic efficiency between cycling. Our comparative study of solid electrolyte interphase (SEI) formation in the carbonate-based electrolyte with and without VC additive revealed that in the pristine electrolyte SEI consists mostly of inorganic components whereas adding VC introduces a polymeric organic component to the SEI increasing its elasticity and stability against fracturing upon HC expansion/contraction during electrochemical cycling. In a pristine carbonate-based solution, the SEI layer starts to form when electrolyte components (solvent molecules and salt anions) decompose on the HC surface. We assume that the subsequent intercalation of K^+-ions results in the particle expansion and the SEI cracking. Freshly exposed HC surface react with the electrolyte components forming new SEI that further diminishes the CE values. When VC is added, its reduction shifts the SEI nucleation potential to lower values as compared with the pristine electrolyte solution and changes its composition.

The findings of this study suggest that the modified SEI layer with more polymeric components possesses higher elasticity and survives the HC expansion/contraction during K^+ intercalation/ deintercalation.

Study of metal ion battery materials, surface layer formation at the electrode/electrolyte inteface and degradation processes during battery operation

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Towards Lithium-Sulfur Microbatteries: Challenges and Recent Progress

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The demand for high-performance energy storage devices is increasing as the need for portable and sustainable power sources grows. Lithium-Sulfur (Li-S) batteries have emerged as a promising alternative to traditional lithium-ion batteries (LIBs) due to their high theoretical specific capacity, energy density, low cost, and environmental friendliness. However, the development of Li-S microbatteries is still in its early stages due to limited research on sulfur thin-film cathodes.

To achieve the desired electrochemical characteristics of Li-S batteries, challenges such as the "shuttle effect" caused by the dissolution of intermediate lithium polysulfides and degradation of lithium anodes need to be addressed. Carbon additives, including multiwall carbon nanotubes (CNTs), have proven effective in enhancing Li-S battery performance by improving conductivity and preventing active material loss. The selection of appropriate electrolytes, such as solid polymer electrolytes (SPEs), can address safety concerns and improve Coulombic efficiency.

The study presented in this paper introduces an efficient, simple, low-cost, and high-performance approach for obtaining a thin-film sulfur cathode for Li-S microbatteries. The cathode material is synthesized through mechanochemical processes and coated with a polymer layer to enhance stability and prevent active material dissolution. The spin coating technique is employed to deposit a thin film of the cathode material onto a conductive substrate, resulting in a uniform and controlled electrode surface.

Comprehensive characterization of the synthesized cathode material using various analytical techniques demonstrates excellent electrochemical performance. The polymer-capped sulfur-CNT cathode exhibits high specific capacity, cycling stability, and rate capability. This research contributes valuable insights to the development of high-performance Li-S microbatteries and highlights the potential of the polymer-capped sulfur-CNT cathode for practical applications in energy storage.

Overall, this study provides a significant step forward in the advancement of Li-S microbatteries, offering a simple and scalable production method for S-based cathode materials with improved performance characteristics. The findings have implications for the development of more efficient and sustainable energy storage solutions to meet the growing demands of various applications.

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Biomass-derived porous carbon decorated with NiO nanoparticles for lithium-sulfur batteries

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Lithium-sulfur batteries (LSBs) are recognized as the next-generation energy storage systems in view of their extremely high theoretical specific capacity (1675 mAh g^{-1}) and theoretical energy density (2600 W h kg^{-1}) [1]. However, the major drawbacks commonly associated with low sulfur electrical conductivity, cathode's volume expansion during cycling and irreversible lithium polysulfides shuttle still significantly limit their practical application [2].

To overcome these drawbacks in the current work the highly porous and conductive carbon matrix was developed from the natural biomass source (rice husk) by carbonization and thermo-chemical activation methods, which was further applied as a matrix for fabrication of the cathodes by sulfur immobilization via melt-diffusion process. The studies revealed that the specific surface area of the biomass-derived carbon is higher than 2200 m^2 g^{-1}, the average pore size is in the range from 2 to 4 nm and its consists of the few-layered graphene-like structure. After sulfur immobilization the specific surface area decreased drammaticaly to nearly 200 m^2 g^{-1} confirming the successful sulfur encapsulation in the pores of the carbon. The prepared carbon and carbon/sulfur cathode material were characterized by various techniques including SEM, SEM-EDS, TEM, Raman-spectroscopy, TGA, XPS, BET.

Further, to suppress the lithium polysulfides shuttle effect the prepared carbon was decorated with NiO nanoparticles using NiNO$_3$ aqueous solution. As a result, the homogenious distribution of the NiO particles with an average size of less than 40 nm was achieved and this composite is characterized by the synergistic effect for lithium polysulfides physical trapping (carbon) and chemical confinement (polar NiO).

The electrochemical performance of the prepared cathode materials was investigated. The CR2032 coin-type cells were used for conducting electrochemical measurements. The cell consisted of the developed carbon/sulfur cathode with an areal sulfur loading of nearly 1.5 mg cm^{-2}, Li metal as an anode and commercial Celgard separator modified with carbon/NiO composite. The lithium bis-(trifluoromethane) sulfonamide (LiTFSI, 1 M) with lithium nitrate (LiNO$_3$, 2 wt.%) in 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1, v/v) was applied as an electrolyte.

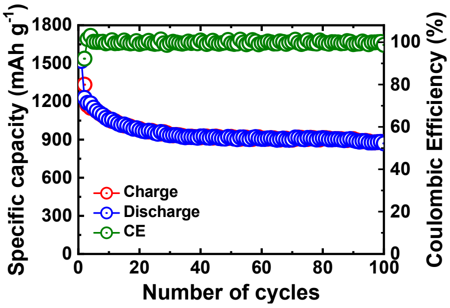

Figure 1. Cycling performance of the assemled cell

As a result, the cell based on biomass-derived/sulfur cathode combined with carbon/NiO modified separator delivered high initial discharge capacity of 1511 mAh g^{-1} at 0.2 C with the capacity retention of nearly 70% from the 3rd cycle. The first 3 cycles are responsible for the stabilization of the battery during which the SEI is formed and the cell is completely stabilized. The Coulombic efficiency of the cell is around 98% over 100 cycles. The cells are under the continious investigation at the moment.

In summary, replacing expensive commercial carbons like graphene, CNTs, and fullerenes with cost-effective biomass carbon is a promising approach for developing practical LSBs. However, further research is necessary to explore sulfur immobilization methods, separator modification, electrolyte customization, and anode protection.

Acknowledgement

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Comparison of 0-D vs 1-D electrochemical models to predict the impact of electrolyte properties on lithium-sulfur battery performance

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Due to its high theoretical gravimetric and volumetric energy density, lithium-sulfur (Li-S) batteries have attracted much interest as beyond Li-ion batteries in the past few years. Besides, sulfur is abundant in nature, non-toxic to the environment, and cheap. The kinetics involved in the cathode of Li-S battery is highly complex and generates several intermediate species soluble in the electrolyte.[1] Since the electrolyte design significantly affects the energy density, it has to be deeply investigated. In this work, one-dimensional,1-D, and zero-dimensional, 0-D, models are constructed to compare their capability of capturing the influence of electrolyte properties on the discharge capacity. Both models have the following 5 electrochemical reactions and 2 precipitation/dissolution reactions.

$$0.5S_8^0 + e^- \leftrightarrow 0.5S_8^{-2} \qquad (1)$$

$$1.5S_8^{-2} + e^- \leftrightarrow 2S_6^{-2} \qquad (2)$$

$$S_6^{-2} + e^- \leftrightarrow 1.5S_4^{-2} \qquad (3)$$

$$0.5S_4^{-2} + e^- \leftrightarrow S_2^{-2} \qquad (4)$$

$$0.5S_2^{-2} + e^- \leftrightarrow S^{-2} \qquad (5)$$

$$S_{8\,(s)}^0 \leftrightarrow S_8^0 \qquad (6)$$

$$2Li^+ + S^{-2} \leftrightarrow Li_2S \qquad (7)$$

The 0-D model is based on Zhang et.al, [2] and the 1-D model is based on Kumaresan et al.[3] model. Both models are solved in FORTRAN after the necessary linearization, according to the block tri-diagonal matrix algorithm. Sensitivity analysis is done to understand how electrolyte properties affect the variables in the model.

Figure 1 shows how the diffusion coefficient affects the discharge profile. As clearly seen in the figure, increasing the diffusion coefficient doesn't lead to any significant change, whereas decreasing the diffusion coefficient results in a reduction in capacity. Up to 0.01 fold, the 1st plateau capacity doesn't change; however, further decrease leads to a decrease in the 1st plateau capacity. This may be caused by sulfur dissolution kinetics being greatly affected. The effect of change of ks8 is illustrated in Figure 2. Increasing the ks8 doesn't lead to a capacity change in the 1-D model, while it leads to a decrease in capacity in the 0-D model. Decreasing ks8 in the 1D model results in a capacity reduction, while it does not affect the capacity in the 0-D model.

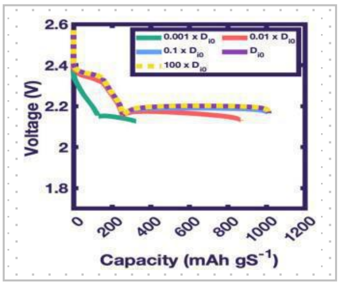

Figure 1. Sensitivity of the predicted discharge profiles on the diffusion coefficient in the 1-D model

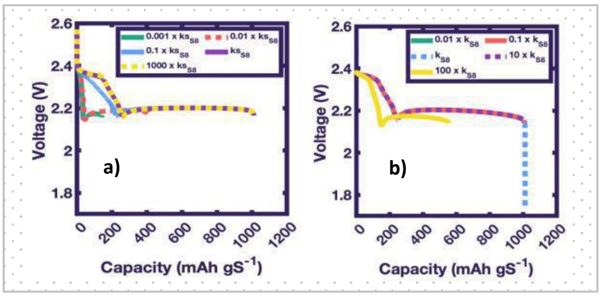

Figure 2. Sensitivity of the predicted discharge profiles on the S8 precipitation constant in the (a) 1-D and b) 0-D models

Acknowledgments

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Synthesis and Study of Composite Aerogels Based on Graphene Oxide and MXene for Lithium-Sulfur Batteries

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Lithium-sulfur (Li-S) batteries have attracted considerable attention due to their high theoretical energy density, low cost, and environmental friendliness. However, their practical application is limited by sulfur's low conductivity and polysulfides' shuttle effect. To overcome these limitations, composite materials have been widely studied.

Graphene oxide (GO) has shown potential in serving as an electrode material due to its exceptional chemical stability and mechanical flexibility. It has the ability to be transformed into a 3D porous aerogel through a hydrothermal process followed by freeze-drying [1].

Recently, a new type of 2D material called MXenes has gained attention for its potential use in energy storage systems. Among the different types of MXenes, those based on titanium have been extensively researched and are being considered hosts for sulfur in Li-S batteries due to their highly polar 2D structure and excellent conductivity. Due to the similarities in their two-dimensional structure, it is highly advantageous to combine $Ti_3C_2T_x$ MXene and rGO in order to create a three-dimensional, porous aerogel with a highly efficient two-dimensional polar adsorption interface.

The fabrication of three-dimensional nitrogen-doped graphene oxide was achieved by combining one-pot hydrothermal assembly and followed a freeze-drying technique [1]. This method applies ethylenediamine (EDA) as a nitrogen source and 3D graphene structural modifier. Mxene was produced via the Wet Chemical Route which uses HF to remove "A" layers from the MAX phases[2].

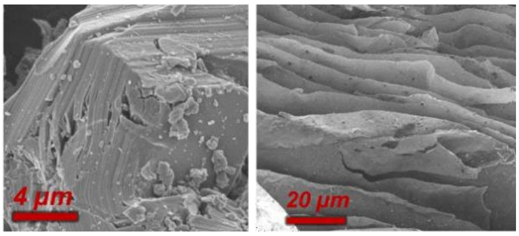

Figure 1. SEM images of Max-phase on the left and Mxene on the right

Mxene@S, rGO@S, and Mxene/rGO@S composites are synthesized and characterized them by SEM, TEM, and XPS. We have successfully removed "A" layers from the MAX phases which are shown in SEM images.

The CR2032 coin-type cells are used for conducting electrochemical measurements. The homogeneous slurry was coated on carbon-coated aluminum foil to prepare a cathode, which consists of synthesized composites mentioned above (80 wt%), conductive acetylene black (10 wt%), and polyvinylidene fluoride binder (10 wt%) all of which are dispersed in N-methyl-2-pyrrolidone. The as-prepared cathode, Mxene/rGO@S exhibited an initial discharge capacity of 918.11 mAh/g and maintained a capacity above 800 mAh/g after the 15th cycle, demonstrating its potential as a promising material for Li-S batteries.

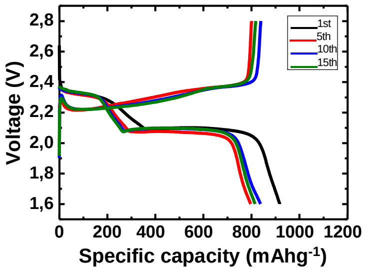

Figure 2. Galvanostatic charge-discharge profiles of Mxene/rGO@S composite (under cycling)

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Experimental characterization of the effect of the electrolyte-to-sulfur ratio on the Li-S battery performance for different electrolyte systems

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Along with the increase in demand for electric vehicles recently, lithium-sulfur (Li-S) batteries have been a top research topic due to their high theoretical specific energy and energy density, which differ them from commercial batteries [1]. However, these batteries that are promising options for the future are still in the research phase because there are some crucial obstacles that must be overcome, such as the polysulfide shuttle mechanism, capacity fade, etc., resulting from the complex mechanisms in the batteries.

There are several solutions to deal with these problems. One of the best ways for this purpose is electrolyte design because the electrolyte-to-sulfur (E/S) ratio, which is a crucial cathode design parameter, plays a significant role in the performance of the Li-S batteries. An increase in the E/S ratio affects the voltage and the capacity of the cell positively while mitigating the system-level energy density and specific energy of the cell [2,3]. In this regard, comprehension of the effect of the electrolyte-to-sulfur ratio on battery performance might enable researchers to shed light on overcoming these problems.

In this study, the characterization of the effect of the E/S ratio on the Li-S battery performance for different electrolyte systems is experimentally studied. Previously in the literature, the most common electrolyte, which is 1M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in a mixture of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) at a volume ratio of 1:1, was used in order to investigate the effect of the E/S ratio on battery performance [2,3]. Here, we investigated the impact of the E/S ratio for five different electrolyte systems; 1M LiTFSI or trifluoromethanesulfonate (LiTF) in triethylene glycol dimethyl ether (G3) and 1M LiTFSI, LiTF, or lithium perchlorate ($LiClO_4$) in sulfolane electrolytes were used in order to investigate the effect of the E/S ratios of 6, 9, 16, and 23 mL/g on Li-S battery performance.

As a result, it can be clearly seen in Figures 1a and 1b that in electrolytes with LiTFSI in Sulfolane or G3, the highest capacity is observed at an E/S ratio of 9 mL/g. On the other hand, for sulfolane with 1M $LiClO_4$, an E/S ratio of 6 mL/g has the highest capacity (Figure 1c). Also, the discharge capacity is high at an E/S ratio of 6 mL/g in G3 with LiTF, as seen in Figure 1d. It is concluded that unlike the LiTFSI in DOL:DME electrolyte system, Li-S cells with sulfolane or G3-based electrolyte systems achieve high discharge capacities at low E/S ratios. On the contrary, the capacity retention for all electrolytes is limited.

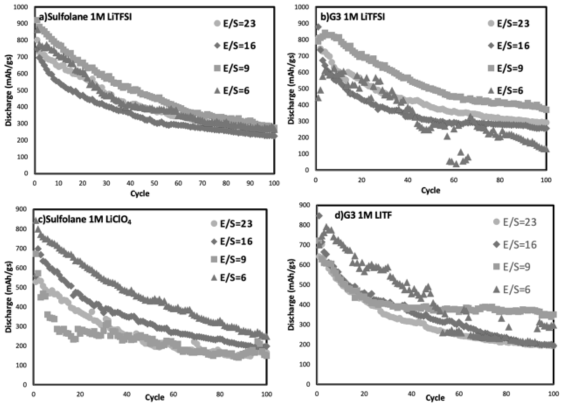

Figure 1. Effect of E/S ratio on the discharge capacity profiles of Li-S cells with a) 1M LiTFSI in Sulfolane, b) 1M LiTFSI in G3, c) 1M $LiClO_4$ in Sulfolane, and d) 1M LiTF in G3 electrolyte systems.

Acknowledgments

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Synergistic effect of Ni/TiO_2 heterostructures on performance enhancement of lithium-sulfur batteries

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Lithium-ion batteries (LIBs) opened new opportunities for rapid development of modern portable devices. LIBs use mainly the intercalation cathodes represented by transition metal oxides and phosphates as cathodes, which are incapable of fulfilling the requirements of electric vehicles and high energy storage systems due to their limited energy density (less than 400 W h kg^{-1}). Moreover, intercalation type cathodes have several drawbacks associated with high cost of materials and safety issues which also limit their use in electric vehicles and large-scale power systems. Therefore, implementation of alternative systems with higher specific capacity, energy density and inexpensive sources is required to meet high demands. In this regard, lithium sulfur (Li-S) batteries are considered as one of the most promising energy systems due to high theoretical specific capacity, which results in a theoretical energy density of 2600 Wh kg^{-1}[1]. Moreover, sulfur has low cost, considerably less environmentally impact and abundant resources [2]. However, the implementation of Li-S batteries is hindered due to several drawbacks such as low conductivity of sulfur, complicated redox reactions, shuttle of soluble intermediates (polysulfides, LiPS), dendrite growth on lithium anode and volumetric expansion of cathode upon reduction to Li_2S_2/Li_2S which leads to structural degradation and lower the cycle life of batteries [3].

The shuttle effect can be suppressed via encapsulation of sulfur into carbon matrices, synthesis of conductive sulfur composites with polymers, etc. In our recent works we reported on carbon materials with metal -oxides, -sulfides and -nitrides as sulfur immobilizers exhibiting strong affinity to LiPSs. Despite such strong immobilization effect of metal compounds, the conversion of sulfur to the end products needs to be enhanced by introduction of electrocatalysts. In this work, the synergistic effect of heterostructures with double functions, titanium dioxide as LiPSs immobilizer with Ni nanoparticles as electrocatalysts were prepared and analyzed as an effective sulfur host material.

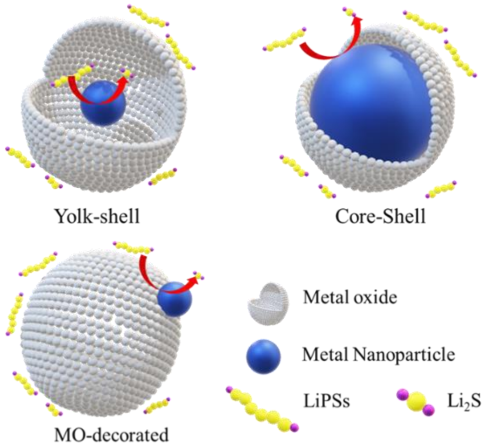

Figure 1. The histogram illustrates the possible structure of Ni-TiO_2 composite compounds.

The present study focuses on the implementation of composite compounds with dual effects on the performance enhancement of Li-S batteries.

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Polyacrylamide/PEDOT: PSS based Hydrogel as an Electrolyte for Aqueous Zinc Ion Battery Systems

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As demand for aqueous zinc-ion batteries (AZIBs) continues to rise, it's important to consider the drawbacks of their current electrolyte solution. AZIBs commonly use a zinc salt solution as an electrolyte and a cellulose or nylon paper as a separator, but this solution can leak or crystallize due to water evaporation, leading to decreased conductivity. However, hydrogel electrolytes [1] may offer a solution to this problem, with their high water-encapsulation and unique properties based on the polymer structure, such as stretchability, self-healing, and thermal sensitivity [2, 3]. It's crucial to develop environmentally friendly, safe, and low-cost electrolyte systems to enhance the potential of AZIBs for commercial use.

In this study, a polyacrylamide and poly (ethylene dioxythiophene): polystyrene (PEDOT: PSS) (PPP) based hydrogel electrolyte was successfully synthesized (Fig 1.a) and characterized. The results showed that adding PEDOT: PSS increased the polymer's water uptake and swelling ratio (Fig. 1.b), indicating better water encapsulation and stability of the polymer structure.

The SEM images (Fig. 1.d) revealed a porous structure with an average pore size of 2.15 µm, suitable for electrolyte and separator functions. Cyclic voltammetry (CV) (Fig. 1.c) was performed to assess the potential working window of the hydrogel electrolyte. The results showed that the PPP hydrogel-based electrolyte exhibited improved performance compared to other electrolytes, suppressing oxygen evolution with the enhanced electrochemical potential window up to 2.45V. The effects of different concentrations of salts and solvent additives were also studied, demonstrating the potential of the developed hydrogel electrolyte for AZIBs.

Additionally, characterization techniques such as Fourier transform infrared spectroscopy (FTIR), electrochemical impedance spectroscopy (EIS), and voltage polarization of the Zn/Zn symmetric cell with PPP and PAM hydrogel electrolyte were employed to evaluate the properties of the hydrogel electrolyte, indicating improved stability, better conductivity, and structural integrity due to the addition of PEDOT: PSS. The study concludes that the PEDOT: PSS-based hydrogel electrolyte is a promising candidate for use in aqueous battery systems, providing enhanced electrochemical performance and expanding the working potential window.

Acknowledgements

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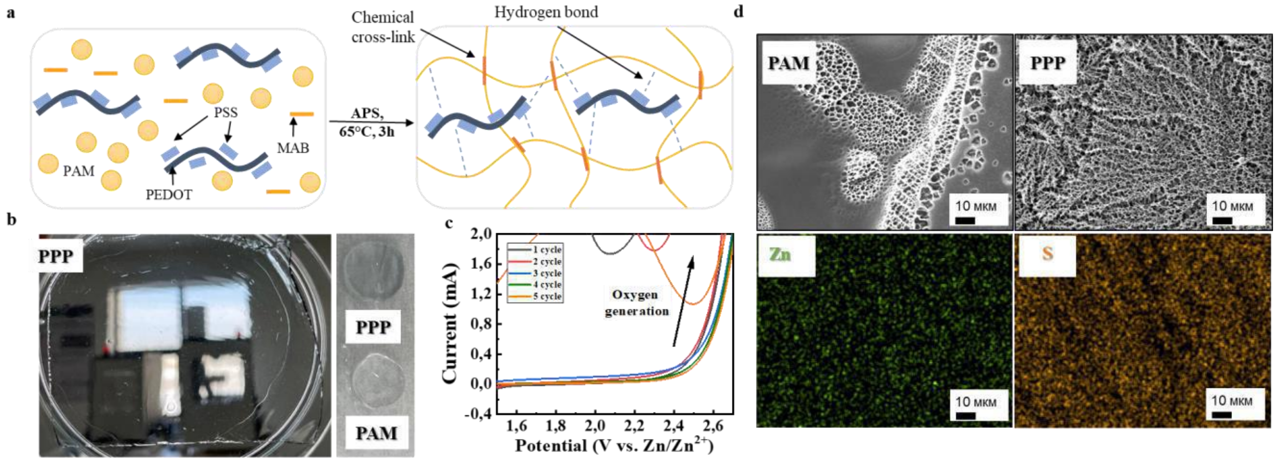

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Puckered V_2O_5 polymorph as cathode material for Rechargeable Aqueous Hybrid-ion Batteries

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The ideal battery could be one combining the stability and energy density of LIBs with the advantages of zinc aqueous batteries, which could remarkably reduce the cost of the energy storage. Therefore, the development of high energy density and ecologically friendly aqueous hybrid-ion battery technology is crucial. More recently, Rechargeable Aqueous hybrid ion batteries (RAHBs) design attracted great interest due to the high operating voltage, low cost and high-power density compared to traditional Li and Zn aqueous batteries [1], [2]. The main difference from typical "rocking-chair" type, RAHBs operate based on two electrochemical redox processes separately on anode and cathode.

In previous works, hybrid system Zn/α-V_2O_5 in 4M $ZnSO_4$ + 3M Li_2SO_4 (pH=4) was reported with investigation of structural mechanisms upon discharge/charge process. At 1C, a capacity of 80 mAh g^{-1} is outstandingly stable over more than 300 cycles with a capacity retention of 100 %. Strong similarities with the well-known structural changes reported in nonaqueous lithiated electrolytes are highlighted, although the emergence of the usual distorted δ-LiV_2O_5 phase is not detected upon discharge to 0.8 V. The pristine host structure is restored and maintained along cycling with mitigated structural changes leading to the high capacity retention. The present electrochemical and structural findings reveal a reaction mechanism mainly based on Li+ intercalation, however co-intercalation of a few Zn^{2+} ions cannot be completely dismissed. The presence of zinc cations between the oxide layers may act as pillars to stabilize the structure upon the cycling [3].

Besides stable α-V_2O_5 phase another metastable γ'-V_2O_5 polymorph exists [4], [5]. The puckered layers of γ'-V_2O_5 allow reversible Li insertion in higher voltage window (3.6/3.5 V vs. Li+/Li) than α-V_2O_5 (3.4/3.2 V vs. Li+/Li). The layered structure of γ'-V_2O_5 consists of infinite ribbons made of VO_5 edge-sharing distorted pyramids leading larger interlayer spacing enables to accommodate large amount of guest cations (5.02 Å in γ'-V_2O_5 against 4.37 Å). Therefore, it attracts the current attention as cathode material for Li, Na-ion batteries in organic electrolyte.

However, in spite of attractive structural features, γ'-V_2O_5 phase has been never studied in aqueous batteries with hybrid electrolyte. In this work, for the first time the electrochemical and structural investigations will be provided in Zn /2.5M Li_2SO_4 + 3.4M $ZnSO_4$/γ'-V_2O_5 system (Figure 1).

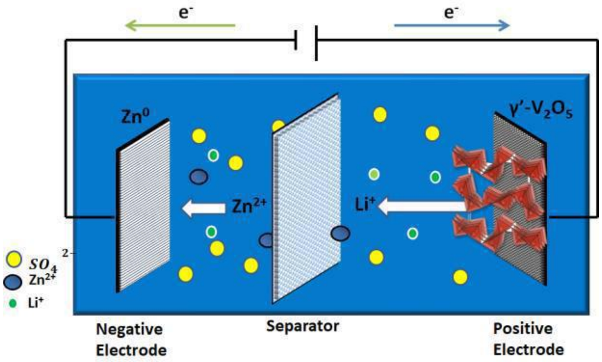

Figure 1. Schematic mechanism of Zn/2.5 M Li_2SO_4 + 3.4 M $ZnSO_4$/γ'-V_2O_5 system

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Promising anode materials for Ni-MH batteries and alkaline fuel cells

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Modern metal hydride power supplies are considered reliable and safe in operation, with relatively high energy efficiency and low cost manufacturing. Nickel-metal hydride (Ni-MH) batteries are widely used in portable electronic devices due to their high energy storage density, overcharging resistance and good environmental compatibility. Alkaline metal hydride fuel cells can also operate at near normal temperatures and do not require expensive catalysts.

Various intermetallic compounds (IMC) of the AB_5, $AB_{3-3.5}$, and AB_2 types are widely used as working materials for metal hydride power sources [1]. AB_5 type compounds have high catalytic activity and cyclic stability, but their electrochemical capacity is limited. AB_2-type IMC have higher capacitive characteristics compared to traditional AB_5-type IMC, $AB_{3-3.5}$ also show a higher electrochemical capacitance, but their cyclic stability is greatly reduced during oxidation and corrosion in an alkaline electrolyte.

The use of new Mg-containing alloys $(La,Mg)Ni_3$ (AB_3-type) and $(La,Mg)_2Ni_7$ (A_2B_7-type) with a high capacity instead of traditional $(La,Mm)Ni_{5-x}Ti_x$ (AB_5-type) served as a significant incentive for the next wave of research development. Cheaper manufacturing of carbon structures (graphene, carbon nanotubes and nanofibers) contributed to the creation of a large range of new composite materials with high performance characteristics. Work on the formation of new alloys, composites and technologies for their processing is carried out all over the world, and the number of publications is increasing exponentially. In addition, the increase in the cost of raw materials, the deterioration of the environmental situation in the world, the rise in the cost manufacturing technologies and the tightening of safety requirements make it possible to consider metal hydride power sources as an important alternative to lithium-ion sources.

The staff of the complex of laboratories for hydrogen materials science of the FRC PCP MC RAS is actively investigating the hydrogen sorption and electrochemical characteristics of new promising composite materials for reversible hydrogen storage and metal hydride power sources [2–4]. In the course of the research, intermetallic compounds of the AB_5, $AB_{3–3.5}$ and AB_2 types were studied. It has been shown that AB_5 intermetallic compounds based on lanthanum are relatively easy to activate, they have high kinetic characteristics and good cyclic stability. Partial replacement of La by lighter Mg, as well as by other rare earth elements in $(La,Nd,Mg)Ni_3$ intermetallic compounds with the $PuNi_3$ structure, leads to an increase in hydrogen and electrochemical capacity by more than 20% compared to $LnNi_5$. The capacity of electrodes using $La_{1.5}Nd_{0.5}MgNi_9$ reached 400 mAh/g at a discharge current density of 100 mA/g. AB_2 type intermetallic compounds with the Laves phase structure demonstrate high performance characteristics and cyclic stability, which makes them promising materials for electrodes of metal hydride power sources. The electrodes based on the studied alloys are quickly activated and reach the maximum capacity (370 mAh/g at 100 mA/g) by the fourth charge-discharge cycle. To improve the electrical conductivity of electrode materials, primarily cathode materials, composite materials with additives of carbon nanostructures (nanotubes, nanofibers, graphene-like material) were obtained. It is shown that the electrical conductivity of $Ni(OH)_2$ with carbon nanostructures (3 wt %) is much higher than that of hydroxide with graphite. A technique for the formation of composites by synthesizing nickel hydroxide directly on the surface of carbon nanostructures by precipitation from an aqueous solution of nickel nitrate with ammonium hydroxide was developed. This method made it possible to obtain composites with electrical conductivity an order of magnitude higher than mechanical mixing, and the specific capacity of the electrodes was increased by more than 30% (265 mAh/g).

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Search for Cobalt Free $Ni(OH)_2$ Cathodes for NiMH Batteries

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$Ni(OH)_2$/NiOOH redox couple is used as the cathode in NiMH and many other battery systems. However, development of a high functioning cathode is a bottleneck for this technology. Because, the active material has a 3.0-3.5 eV of band gap [1]. Therefore, it is an insulating material and conductivity must be imparted with additives. Adding cobalt based compounds as conductive additive is the commercially used remedy to this problem [2]. Even though, Co based compounds works well due to formation of continuous and homogeneous network [3], their high cost raise interest toward cheaper options like carbon derivatives. Different carbon based materials are investigated to impart conductivity to the cathode active material [4]. Although, some success has been obtained with these materials, they are not commercialized yet. Being low density and hydrophobic, it is difficult to prepare a homogenous blend of carbon and $Ni(OH)_2$ which adversely effects the electrochemical properties [5].

This study investigates the electrochemical properties of cathodes prepared with two different carbon based materials i.e. carbon black and plasma black. During the blending of the materials two different techniques are used. The first technique is ball milling the powders together to form a homogenous mixture before slurry preparation. And, the second one is the so called dispersion method in which $Ni(OH)_2$ is dispersed in DI water and carbon derivatives are dispersed in ethanol-DI water mixture. Positive charge accumulates on the surface of the $Ni(OH)_2$ and negative charge accumulates on the surface of carbon particles. Combining the two dispersions together while stirring and evaporating the liquids, blending of the carbon and the active material is achieved with electrostatic attraction between the particles.

A reference battery is also prepared by ball milling $Co(OH)_2$ with $Ni(OH)_2$ and then preparing a slurry. The full theoretical capacity of 289 mAh/g is achieved with this battery. Best performing battery is obtained when carbon black and plasma black are used together and dispersion method is employed and 228 mAh/g capacity is attained. However, this capacity wasn't stable and a capacity decay is observed for the batteries prepared with carbon derivatives unlike the reference battery.

Observation of the XRD patterns of the cathodes at different cycles shows that the unwanted γ-NiOOH formation occurs for the batteries prepared with carbon derivatives. XRD pattern of the reference battery revealed no γ-NiOOH formation during cycling. Reaching lower capacity values and having a capacity decay with cycling is attributed to the formation of this phase.

Charge profiles are studied and it is seen that charging potentials were higher for the batteries produced with carbon. And, there was no apparent difference between the oxidation reaction of $Ni(OH)_2$ and oxygen evolution reaction. This difference was quite prominent for the reference battery. Cyclic voltammetry is used to investigate these reactions and same result was obtained. The oxidation reaction and oxygen evolution reaction was well separated for the reference battery and there was an overlap of these reactions for the batteries prepared with carbon derivatives.

The formation of the γ-NiOOH phase is attributed to overlap of competing oxidation and oxygen evolution reactions. Moreover, this overlap is thought to be due to the higher polarization of the batteries. This is under investigation with impedance measurements.

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Development of multi-component Mg-based AB alloy for Ni-MH Batteries

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It is becoming more and more important for decarbonization all over the world.(Cano et al., 2018; Fetcenko et al., 2007; Markolf et al., 2006)Today, fossil fuels are used in many vehicles, especially in the transportation sector. Although many electric vehicles continue to be developed, batteries with high energy density are also needed for these vehicles.

To meet this high energy need, rechargeable batteries with high energy density come to the fore. As an example of these batteries, Mg-based Nickel Metal hydride batteries come to the fore. These batteries stand out with their environmental compatibility and high charging capacity. (Rao & Wang, 2011; Wan et al., 2019) An interesting development within the interstitial hydrides relates to AB alloy with prototype MgNi CsCl structure). Recently, Mg-Co (Zhang et al., 2005), Mg-Ti (Asano et al., 2009), Mg-Ni (Shao et al., 2009), Mg-Ni-B (Shao et al., 2009) and Mg-Tm-V (Tm: transition metals) binary and ternary alloys have been successfully achieved with AB structure. In a binary alloy with a composition MgCo, 3 wt % was reported.

The concept of "high entropy alloys" which attracts great attention has modified the alloy design significantly. In this concept, rather than using the classical alloys which are based on a base metal with added alloying elements a new alloy design concept in which the alloying elements are much higher and nearly equimolar. These high entropy alloys are sometimes called multi-component alloys especially if the components are non-equimolar. Preparing Mg-based alloys with some other capable to store hydrogen alloys or metals with high catalytic activity or better anti-corrosion capability is an approach to improve the performance of Mg-based anodes in NiMH batteries.

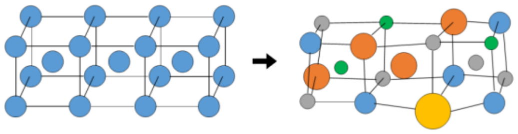

Figure 1. Simple illustration of the effect of multi-component alloying on the lattice distortion of a BCC crystal structure. (Sahlberg et al., 2016)

This study aims to develop Mg-based High-entropy alloys and rechargeable batteries with high charge-discharge capacity by appropriate electrochemical methods have the highest conductivities will be produced in the form of bulk discs and hydrogen permeability performance tests would be performed.

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Carbon nanofibers/reduced graphene oxide aerogels – investigations of the nanofibers loading on the electrochemical performance in aqueous electrolyte

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Graphene-based materials have attracted considerable attention in the field of energy storage due to their exceptional physical and electrochemical properties. Among various forms of graphene materials, graphene aerogels have emerged as particularly promising candidates for supercapacitor applications due to their unique structural properties, high specific surface area, and exceptional electrical conductivity [1]. However, the intrinsic limitations of reduced graphene oxide in the form of an aerogel, such as its low volumetric energy density, impede its practical application in energy storage devices. On the other side, carbon nanofibers (CNFs) are well-known carbon nanomaterials with high conductivity and mechanical robustness, though their low specific surface area limits their use in electric double layer capacitors (EDLCs) [2,3].

In this investigation, we prepared a series of carbon-carbon composites composed of CNFs and reduced graphene oxide (rGO) in the form of aerogels, which were synthesized using a simple, one-step hydrothermal method, followed by freeze-drying to produce highly porous and lightweight structures. The resultant graphene aerogel-CNF composites displayed a hierarchical network with enhanced mechanical strength and electrical conductivity.

Porous structure determined by nitrogen sorption at 77 K revealed developed porosity, with a significant contribution of mesopores due to the nature of rGO aerogel. Furthermore, no direct influence of the CNFs loading on the composite porous structure was observed. The specific surface area of the investigated materials was up to almost 500 m^2/g.

We analyzed the composites' electrochemical performance as electrode materials for aqueous alkaline supercapacitors. Measurements were performed in a three-electrode Swagelok® cell in a 6 M KOH electrolyte. Electrochemical measurements revealed that the graphene aerogel-CNFs composites exhibited high specific capacitance and outstanding rate capability. The specific capacitance of the composites was in the range of 170 to 193 F/g at a scan rate of 10 mV/s. Furthermore, the CNF/rGO composite with 15 wt.% of the CNFs exhibited almost 95% of its initial capacitance when the scan rate increased from 0.5 to 100 mV/s. The enhanced performance is attributable to the synergistic effects of the highly conductive CNFs, which facilitate efficient electron and ion transport within the composite structure, and the high surface area of graphene aerogels for electrochemical reactions.

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Search for New Cathode Compositions for Mildly Acidic $Zn-MnO_2$ Batteries

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Manganese oxide has been used extensively since the invention of batteries. Structurally modified MnO2 is an appealing material for making primary Zn-MnO2 batteries not only rechargeable but also capable of improving the voltage profile. Moreover, Mn and Zn are attractive materials due to their abundance and low cost. Zn/MnO2 batteries could be well-suited for grid energy storage systems, making them more widely used. To achieve this goal, modifying the MnO2 cathode is crucial.

$Zn-MnO_2$ batteries are still being mass-produced as primary batteries. The primary battery cathode active material used is electrolytic manganese dioxide (EMD), which is a form of $\gamma-MnO_2$, and the electrolyte used is aqueous KOH. There is a lot of effort to make these batteries rechargeable by modifying the cathode and the electrolyte. Yadav et al. [1] were able to improve rechargeability and achieve a two-electron exchange by making $Mn(OH)_2$ reversible through the addition of Cu^{2+} and Bi_2O_3. Hertzberg et al. [2] studied the effect of mixing alkaline electrolytes KOH and LiOH, and found that a 1M KOH + 3M LiOH aqueous solution was the best electrolyte for a Bi_2O_3-added MnO_2/Zn foil cell. The addition of LiOH prevented the zincate poisoning. Shoji et al. [3] were the first to suggest in 1987 that $Zn-MnO_2$ batteries could be made rechargeable by using a slightly acidic electrolyte due to problems encountered with alkaline batteries. Sun et al. [4] reported that when a mildly acidic electrolyte is used, the mechanism of co-insertion of H^+ and Zn^{2+} is observed. XRD analysis showed that the main reaction during discharge to 1.3V is H^+ insertion, which forms the MnOOH phase, while discharging to 1.0V results in $ZnMn_2O_4$ formation, indicating Zn insertion.

The main objective of this thesis is to discover new compositions of MnO_2-based cathodes for Zn-ion batteries. To achieve this goal, a combinatorial approach was used by utilizing thick film cathodes that were deposited via magnetron sputtering. The system being studied is based on MnO_2 combined with $NaMnO_2$, Bi_2O_3, and NiO. To facilitate the process, four sputter targets were created, with the MnO2 target placed at the center and the other oxides placed in a triangle around it. The substrates placed in a substrate magazine with a triangular geometry, allowing for the deposition of 36 cathodes with distinct compositions in a single sputtering experiment.

In total, 216 cathodes were produced from six experiments. These cathodes were deposited on Ni foil current collectors and were tested using cyclic voltammetry and galvanostatic techniques. Results showed that Mn-rich cathodes performed the best, leading to the selection of three out of the six sets of cathodes for further analysis. The Mn-rich corner of the Bi-Mn-Ni ternary diagram, with varying levels of Na from 0 to 78%, was analyzed based on their capacities, cyclic stability, and discharge plateau potential. Three compositions with discharge capacities exceeding 400 mAh/g were chosen as candidates based on the analysis.

To verify if the selected cathodes can produce the same or similar capacities, they were also prepared using the slurry route. However, the highest capacity achieved using this method was only about 100 mAh/g. Therefore, more work is required to fully explore the potential of the chosen cathodes.

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Activation of MnO_2 Cathode Materials for Alkaline Zn/MnO_2 Rechargeable Batteries

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After the increase in the use of renewable energy sources, there is still need for reliable and effective energy storage systems all around the world. Rechargable alkaline MnO_2 batteries are attractive for their low cost, non-toxicity and safety than other battery applications. To illustrate, alkaline Zn/MnO_2 modelling analyses represents that costs below $50/kWh are highly affordable, and also precursors of both anode and cathodes are highly abundant in Earth's crust [1].

However, the poor rechargeability of mangenese oxide batteries limited their use on the markets. During the subsequent discharge cycles of MnO_2 batteries results in capacity fade due to the formation of irreversible phases.

To improve the performance of MnO_2, Bi^{3+} and Pb^{2+} additives have been tried that could increase the cyclability up to hundreds of cycles. Wroblowa et al. proposed that Bi^{3+} addition may facilitate the stabilization of layered MnO_2 structure which is desirable and reversible phase for alkaline MnO_2 cathode materials[2]. Also, N. O. Darıcıoglu et. al. suggested new combinatorial approach to create layered δ-MnO_2. For this purpose, they produced cathode samples using magnetron sputtering with $NaMnO_2$, NiO, Bi_2O_3, and MnO_2 as targets. This thin film stucture shows different behaviours such as nickel rich region demonstrating a reliable, quite steady charge –discharge behavior but low capacity, bismuth rich region displayed a capacity only in the first cycle and moderately rich Na region showed the best electrochemical performance among the others [3].

The applicability of the combinatorial approach depends on the electrical behavior of pure manganese oxide after the battery structure is formed. Therefore, this study focused on the activation process of pure manganese oxide cathodes for future experiments. Therefore, the main purpose of this study is to active pure MnO_2 cathode in order to optimize the charge-discharge potential ranges and find proper charge-discharge times of the MnO_2 for future combinatorial approach experiments.

The cathode samples tested with a wide range of variety charge- discharge potential limits to find proper intervals. The best performance for cyclic voltammetry can be observed voltage ranges between 1.3V-0.3V and 10 cycle procedure displayed the best performance. Redox reaction peaks are noticeble, peak area increased and seperation between the lines decreased.

For discharge behaviour, 0.3V cut-off and 0.01C rate displayed the best performance. Discharge curves highly noticeable and medium discharge capacities have been observed. (170 mAh/g – 240 mAh/g respectively). 0.1 C rate is too high to observe proper discharge curves. Under the 0.3V, MnO_2 dissolution may occur from the electrode surface. Therefore, 0.3V discharge limit will be the standard for future experiments.

For charge behaviour, charging the samples without any voltage limitation that gives the best result. Optimizations about the charge potential limitation will continue for the future experiments.

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A large format and high performance aqueous rechargeable $LiFePO_4$/Zn battery for stationary energy storage

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Aqueous rechargeable lithium-ion batteries (ARLIB) have gained significant attention for various energy storage applications due to their inherent safety, low cost, and environmental friendliness compared to traditional non-aqueous battery systems. Here, $LiFePO_4$ (lithium iron phosphate) and Zn (zinc) materials were adopted as a positive and negative electrodes, respectively, for the large format ARLIB prototype. In particular, $LiFePO_4$ is known for its high thermal and chemical stability, theoretical capacity of 172 mAh/g, long cycle life, and excellent safety characteristics. Zinc, on the other hand, is abundant, low-cost, and has a high energy density. By utilizing an aqueous electrolyte, this battery chemistry aims to provide a safer and more sustainable alternative to traditional lithium-ion batteries. However, there are some challenges associated with developing high-performance ARLIBs, especially for stationary energy storage applications. Through continuous research and development, it is crucial to optimize the ARLIBs performance characteristics, such as energy density, power density, cycling stability, and calendar life. This can be achieved through material innovations, electrode modifications, and electrolyte advancements [1,2].

In this study, we aimed to design and develop a large format, high performance ARLIB prototype where following key problems were investigated and optimized: firstly, choosing the appropriate aqueous electrolyte composition is essential. It should provide good ionic conductivity while being stable over a wide voltage range. Various additives and salts were investigated to enhance the electrolyte's stability and reduce parasitic reactions on the Zn anode surface. Secondly is Zn dendrite passivation by adopting several scalable methods, such as magnetron sputtering and polymer layer coating. Thirdly is electrode design and engineering of the cathode and anode electrodes for maximizing performance. Strategies such as optimizing particle size, morphology, and coating technologies can enhance the overall electrochemical performance, including capacity, power, and cycling stability. Next step is the choice of separator that is critical for preventing the crossover of ions between the cathode and anode. High-performance separators with good ionic conductivity and mechanical strength are required to ensure efficient ion transport and prevent short circuits. Lastly, the battery's cell design, such as the arrangement of electrodes, current collectors, and packaging, is taken into account to facilitate efficient ion and electron transport, minimize internal resistance, and enable scalability for large-scale energy storage applications.

The present study provides insights into the importance of the extensive research and collaboration between academia and industry entities to address the technical challenges and optimize the performance and commercial viability of ARLIB batteries.

Acknowledgements

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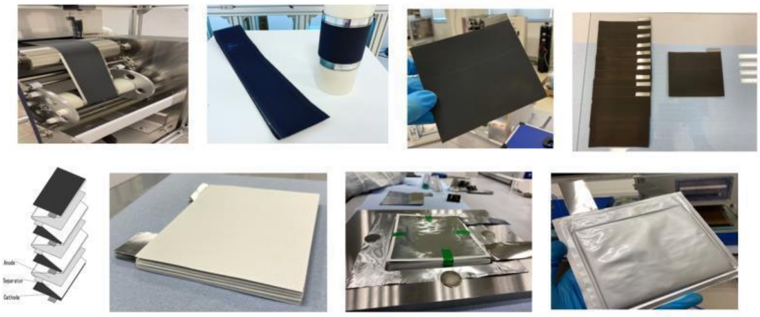

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The elemental cocktail effect of high-entropy spinel oxides on the electrocatalytic performance of zinc-air battery cathode

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Metal-air batteries are heavily dependent on oxygen electrochemical reactions. The oxygen evolution reaction (OER) and the oxygen reduction reaction (ORR) are the key reactions to be catalyzed for improving the energy solution systems, e.g., regenerative fuel cells, water electrolyzers, and zinc-air batteries. Especially OER is the bottleneck of the overall water-splitting reaction due to the sluggish four-electron transfer mechanism.[1-3] Therefore, it is a requirement to catalyze this reaction and upshift the reaction kinetics. However, commercially used iridium oxide (IrO_2) and ruthenium oxide (RuO_2) have poor long-term stabilities and are expensive and scarce.[4] Thus, new, inexpensive, and promising bifunctional electrocatalysts must be designed. High entropy oxides (HEOs) are a new class of promising electrocatalysts due to their unique single-phase and highly disordered structure related to configurational entropy. HEOs are composed of four or five elements on one side with a single-phased crystal structure. The highly disordered structure and high entropy of these compounds cause numerous defective sites and deficiencies, such as oxygen deficiencies; these deficiencies and defective sites act as active sites to catalyze the OER and ORR[5].

In this work, the tetrahedral site of spinel Fe3O4 was changed with different elemental compositions, and the cocktail effect of these elements on the electrocatalytic performance was investigated. Two different types of high entropy spinel oxides (HESOs) were synthesized via the modified Sol-Gel Pechini method; these HESOs are $(MgCoCuNiZn)Fe_2O_4$ and $(MnCoCrNiFe)Fe_2O_4$. The crystal structure of the HESOs was confirmed by X-Ray diffraction (XRD), and the morphology of the samples was observed via scanning electron microscope (SEM). Also, the effect of chemical composition and valence states was determined by X-ray photoelectron spectroscopy (XPS). Electrochemical tests were conducted using a rotating disk electrode (RDE) under an alkaline environment. Afterward, these HESOs were tested as cathodes for rechargeable zinc-air battery by incorporating a zinc-sheet anode and 6 M KOH + $Zn(OAc)_2$ electrolyte in the homemade zinc-air battery cell.

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The Effect of B-site Doping on $NdBaCo_aFe_{2-a}O_6$ (a= 1.8, 1.6, 1.4, 1.2) for Enhanced OER/ORR Activity and Rechargeable Zinc- Air Battery Performance

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Among the numerous electrochemical energy storage technologies, rechargeable zinc-air batteries (RZABs) are increasing in popularity due to their high theoretical energy density, cost-effectiveness, and environmental friendliness[1–3]. However, the lack of effective, reliable, and affordable bifunctional oxygen evolution and oxygen reduction reaction electrocatalysts prevents RZAB's commercialization. Due to its adjustable properties, double perovskite oxides (A2BB'O6) are currently being considered as potential electrocatalysts but the effect of B-site doping to the double perovskite oxides on the bifunctional electrocatalytic activity and their application to the zinc- air batteries as an air cathode are still missing[4,5].

Therefore, in this study we synthesized B-site doped NdBaCoaFe2-aO6 (a= 1.8, 1.6, 1.4, 1.2) electrocatalysts and we investigated their oxygen evolution and oxygen reduction reaction activities. Then, we apply this electrocatalysts to RZABs as an air cathode and measure their capacities and stabilities. Hence, our work demonstrates that changing the elements in the B-site of double perovskite oxides, changes the electrocatalytic bifunctional activity and the Zinc-Air battery performance.

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Carbon-based cathodes for non-alkaline Zn-air batteries: structure-performance relations and stability

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Due to their high theoretical energy density, potentially low cost, and safety, rechargeable zinc-air batteries (ZABs) have been identified as a promising type of energy storage devices. However, research on ZABs has primarily focused on systems with strongly alkaline solutions, which have severe limitations. Anodes in these cells suffer from problems such as uneven plating-stripping of zinc, passivation by zinc oxide, or continuous corrosion in alkaline electrolytes. On the cathode side, irreversible uptake of carbon dioxide from ambient air leads to a decrease in conductivity and clogging of cathode pores with K_2CO_3.

One of the most promising ways to overcome the limitations of alkaline ZABs is switching to non-alkaline electrolytes. The electrolytes with near-neutral pH can substantially improve stability of Zn anodes and circumvent the problem with CO2 absorption from the air. Despite these advantages, non-alkaline ZABs are not well-studied, and the main issue with these batteries is poor kinetics of the oxygen reduction and evolution reactions. Therefore, the development of cathode scaffolds with high catalytic activity in near-neutral media is crucial for non-alkaline ZABs.

Our study focuses on carbon-based cathodes in non-alkaline ZABs that use aqueous solutions of zinc sulfate, acetate or triflate as electrolytes. We explore the relationships between the structure and performance of materials with varying morphology, specific surface area, wettability, graphitization degree and surface chemistry. Additionally, we evaluate the anodic stability of the cathodes using online electrochemical mass spectrometry (OEMS) in combination with Raman spectroscopy and X-ray photoelectron spectroscopy. Our findings offer insights for developing suitable cathodes with attractive morphological and structural characteristics for non-alkaline ZABs.

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Performance of a Homemade Vanadium-Manganese Redox Flow Battery using Electrospun Carbon Electrode Catalyst and its Preliminary System Integration

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Abstract

In this study, the possibility of enhancing the performance of the all vanadium redox flow battery (VRFB) and a vanadium/manganese redox flow battery (V/Mn RFB) using carbonized catalyst layers (CCLs) prepared via electrospinning is considered. To display performance enhancement caused by such catalysts, a home made reactor with non optimized compression and serpentine flow fields was employed. This reactor was manufactured using a combination of recycled metals, graphite and chemically resistant plastic, with serpentine flow fields engraved using in house computer aided manufacture employing SolidWorks software. The surface morphologies of the graphite and carbon based electrodes used during electrochemical tests were characterized by SEM and XRD analyses. For such a non optimized reactor, the application of the CCL as an additional material to an as received graphite felt electrode shows improvements for both vanadium based RFB technologies. For instance, the enhancements in power densities of VRFBs were achieved by 30% improvement in peak power density using CCL. V/Mn flow batteries showed 50% improvement in capacity utilization when using CCL. It is also postulated that because the CCL needs to be placed between the flow fields and the felt electrodes to prevent fiber protrusion into the flow channels when compressed in the reactor, the peak power densities and cycling efficiencies were lower than those reported for optimized RFBs in the literature. The need to improve the power density is a critical consideration for RFBs. A high power density translates into lower capital costs for V/Mn RFBs, which translates into an effective system integration for grid scale load levelling, water desalination or renewable energy storage.

1.Introduction

The vanadium/manganese (V/Mn) redox flow battery can achieve a higher energy density of 35 W h L ^{1} than all vanadium redox flow batteries (VRFBs), owing to its higher cell voltage (1.77 V) [1]. The V/Mn system utilizes V(II)/V(III) redox couples as the negative electrolyte and Mn(II)/Mn(III) redox couples as the positive electrolyte [2].

In spite of the high energy density for the V/Mn RFB, it faces drawbacks owing to Mn^{3+} instability that, in turn, results in precipitation of manganese dioxide thereby causing severe capacity fade [3]. To diminish this problem, a few investigations reported on the use of TiO^{2+} to stabilize the electrolytes [3 5]. Besides the mitigation of manganese dioxide precipitates, both VRFBs and V/Mn RFBs have displayed performance drops due to insufficient electrode wetting of the graphite felt electrodes, thereby suffering from high mass transport polarizations [6]. Thermally or chemically treating the felts provide some performance enhancement [7]


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but a more economically robust means for solving such issues could involve the application of other electrode catalysts involving carbonized nanosheets, graphene or carbon nanotubes [7, 8]. Electrospinning has been employed as an effective means to prepare carbonized fibrous mats [7] to provide enhanced performances in VRFBs [9] and of late in a hydrogen/vanadium hybrid flow battery [10]. However, the application of such nanomaterial electrode catalysts or stand-alone electrodes prepared by means of electrospinning has not been studied significantly for other redox couples and their evaluation for V/Mn RFBs could be a step forward towards investigations with other RFB electrolytes.

In this work, carbonized catalyst layers (CCLs manufactured in-house by means of electrospinning and carbonization) were evaluated in both VRFB and V/Mn RFB systems. The graphite felt control electrode was deliberately not activated thermally or chemically to understand the effect of CCLs in both RFBs. The RFB used herein was homemade in order to consider potential issues that could arise from non-optimised flow field design, electrode compression and other factors. The main reason for using a non-optimized reactor (unlike Scribner ones employed in our previous studies [11]) is to try and highlight the performance enhancements that could be achieved solely by using CCLs and at reduced capital investments. However, low power densities were determined, which result in high costs, due to which more studies are required to improve the electrochemical features of CCL. If that can be successfully achieved, then V/Mn RFBs may be integrated with renewable energies resulting in lower carbon footprints of electricity generation. A brief consideration of this has also been reported herein to emphasize the importance of V/Mn RFBs due to their flexible energy to power ratio as well as a decent control complexity in comparison to other battery technologies (owing to the employment of active elements such as pumps for electrolyte flow) when applied for systems integration for grid-scale electricity generation, storage and supply.

2. Experimental

2.1. Chemicals and Electrolytes

Iron acetylacetonate [Fe(acac)$_3$] was obtained from Sigma-Aldrich (≥97%, Dorset, UK), N,N'-dimethylformamide (DMF, Technical grade for electrospinning, ∼94% pure) was purchased from VWR International (Leicestershire, UK) and polyacrylonitrile (PAN) was sourced from Goodfellow Cambridge Limited Huntingdon (average particle size ∼50 μm, molecular weight ∼230,000 g mol^{-1}). Vanadium (IV) oxide sulfate (hydrated) was purchased from Sigma-Aldrich (purity > 99%, Dorset, UK). MnCO$_3$ (Sigma-Aldrich, ≥99.9% trace metal basis from Dorset, UK) was used as received. TiOSO$_4$ (Sigma-Aldrich from Dorset, UK) was added to the manganese electrolyte solution only to prevent the precipitation of MnO$_2$ as discussed elsewhere [12]. This Mn-Ti electrolyte was used for the V/Mn RFB system. Sulfuric acid (5 M) was obtained from Fluka (Dorset, UK). All chemicals were used without further purifications. All solutions were prepared by using deionized water (18 MΩ) and all chemicals were of analytical grade, where not specified.

2.2. Membrane-Electrode-Assembly (MEA)

A well hydrated Nafion 115 membrane (127 μm thick, Fuel Cell Store, Texas, USA) was sandwiched between both electrodes (anode and cathode) to prepare the membrane-electrode-assembly (MEA). The membrane was pre-treated in 1 M H$_2$SO$_4$ solution for 1 h at 80 °C and then rinsed with de-ionized water. Graphite felts (4.6 mm thick, SGL group, Germany, Sigracell GFD4,6 EA) and CCLs (100 µm thick - homemade) were not pre-treated and used as received for VRFB and V/Mn systems. CCL was made via a combination of electrospinning and carbonization as detailed elsewhere [11].

2.3. Morphological Analysis

The surface morphologies of the graphite and carbon-based electrodes used during electrochemical tests were characterized by SEM analysis. This was performed using a Zeiss Sigma FEG-SEM instrument. XRD was performed using an Aeris desktop machine with data analysis performed by means of Highscore software (Malvern Panalytical).

2.4. Redox Flow Battery Cell Assembly

Battery testing was conducted using a 5 cm^2 single cell (designed in-house). The fabricated VRFB hardware consisted of two aluminium endplates (sourced from workshop waste), copper current collectors (also from workshop waste), and graphite plate with serpentine flow fields (engraved in-house using a computer-aided manufacturing machine, operated via SolidWorks software). The positive and negative electrodes were separated by a Nafion 115 ion-exchange membrane. The electrodes were made of graphite felt at both the positive and negative sides of the cell for investigating classical RFB behaviour. The electrodes were modified by adding CCL on the flow channels with the felts facing the membrane for additional experiments to determine the influence of CCL upon RFB performance. Viton gaskets (J-Flex) were placed between the different parts of the cell to prevent leakage of the electrolyte, and to allow a reasonable compression of the electrode. The entire cell was compressed to 2 Nm torque to avoid carbon felt deformation, without obtruding the flow channels whilst avoiding leaks. This torque was much lower to those applied when assembling commercially sourced Scribner flow cells [11], which could have caused significant performance drops. Higher compressions could ensure better electrode performance but at the cost of blocking the flow channels with graphite fibers and/or CCL fracture (when using them with felt) that could increase pressure drops and mass transport polarizations.

2.5. Experimental Operation for VRFB and V/Mn RFB

All experiments were carried out at 20 °C. The all-vanadium electrolyte was initially made by dissolution of 1 M VOSO$_4$ (99.9% purity, Alfa Aesar) in a sulfuric acid solution of 5 M concentration [12]. Both electrolyte reservoirs initially consisted of a solution of vanadium (IV) ions. The positive electrolyte volume was initially twice the negative electrolyte volume to account for the double electron transfer reaction that is needed on the negative side to convert vanadium (IV) into vanadium (II) ions. These electrolytes were then charged until the vanadium (IV) was fully converted to vanadium (II) and vanadium (V) for the negative and positive electrolytes, respectively. Half of the electrolyte on the positive side was then removed from its reservoir, making the volumes on each side identical for consequent experiments [13]. The negative and positive electrolyte tanks are filled with the prepared electrolyte to a volume of 100 ml and pumped (Cole Parmer Masterflex Model 77200-50) to the negative and positive half cells, respectively. The negative reservoirs were purged with N_2 gas (BOC) and sealed before the single-cell test to prevent oxidation of V(II) in air or via dissolved oxygen.

The galvanostatic tests were performed using a Bio-Logic potentiostat (VSP-300) with a 10 A booster and data logging was performed using EC-Lab software. For all tests, the system was allowed to reach an upper cut-off voltage of 1.8 V and a lower cut-off voltage of 0.8 V for VRFBs. These values were changed to 2.1 V (upper cut-off) and 0.6 V (lower cut-off) when evaluating the V/Mn RFB. This was done to ensure high electrolyte utilization and to try and minimize side reactions such as hydrogen evolution. Several-cycle charge-discharge tests were performed at constant current densities in the range of 20−100 mA cm^{-2} for the VRFB and V/Mn RFB.

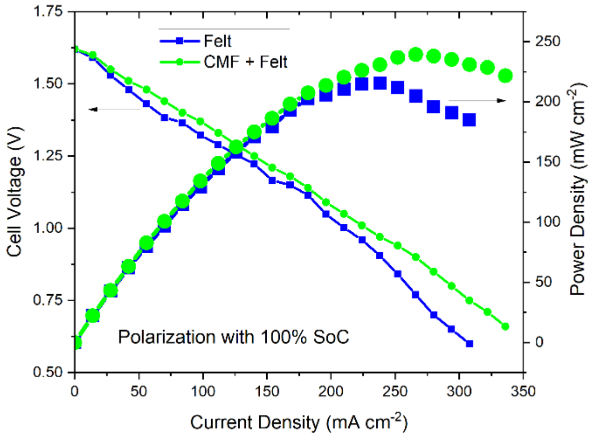
Finally, potential-current density curves were obtained at an initial state-of-charge (SoC) of 100%, by applying steps of galvanostatic discharge at constant current densities in the range of 40−500 mA cm^{-2} (30 s discharge followed by 120 s rest between each discharge step). Cycling was carried out between 50 and 100 mA cm^{-2}. Electrolyte utilization was determined at 80 mA cm^{-2}. Efficiencies were also determined at 80 mA cm^{-2}.

3. Results and Discussion

3.1. VRFB performance using Electrospun CCL and graphite felt electrodes

The power densities of the VRFB using graphite felts and compared with the same system employing CCLs is shown in Fig. 1. The CCL appears to improve the peak power density (almost 250 mW cm^{-2}) by approximately 30% compared to just using the untreated graphite felt (slightly in excess of 210 mW cm^{-2}). A similar performance advantage is also noticed for electrolyte capacity when using the CCL in combination with felt electrodes (Figure 1b, which shows that the cell capacity utilization when using felt electrodes only was less than 200 mA h but this increased to almost 250 mA h when CCL was used along with felt electrodes).

(a)



(b)

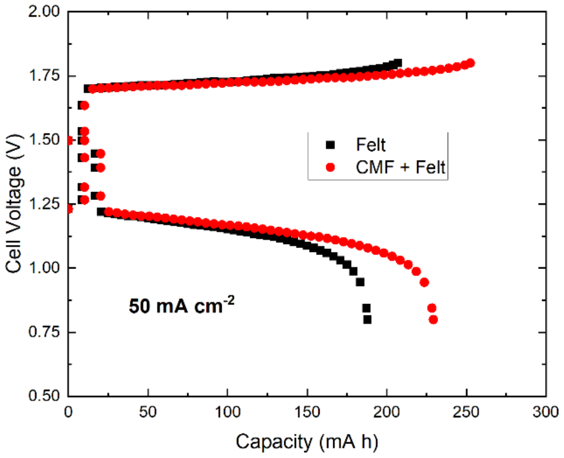


Fig. 1. Polarization and power density curves for VRFB. System condition = 1 M $VOSO_4$ in 5 M H_2SO_4 (initial electrolyte composition), 50 ml min^{-1} flow, 100 ml volume (each), less than 20% electrode compression, room temperature and negative half-cell was maintained with an inert nitrogen blanket to prevent V^{2+} spontaneous oxidation to V^{3+} (which occurs in the presence of oxygen). CCL was placed in between the graphite felt and the flow channels in both half-cells.

The better wetting of electrodes due to the presence of carbon nanotubes (CNTs, present in the hair-like structures of CCLs) may also be deciphered from qualitative morphological analyses as discussed as follows. Fig. 2 shows the XRD patterns for graphite felt samples compared with those of CCL. The peaks associated for graphite felt is identical to that reported in the literature [14]. Also, peaks depicting presence of iron and carbon are prominent for CCL. Additionally, CCL appears to have more disorder than felt due to the presence of hair-like CNTs, which could have contributed to the improved catalytic performance of the material as reported recently for a hydrogen/vanadium hybrid flow battery [11]. Additionally, the SEM images of both carbon materials are provided as insets with their respective XRD images in Fig. 2. CCL has more bundles of fibers along with “hair-like” outgrowths that may improve access of electrolyte to active electrode areas for the vanadium ions to undergo fast charge transfer in comparison to the untreated graphite felt. It seems evident, also from previous studies [14], that CCL is able to catalyze liquid-based redox reactions more effectively when combined with a commercial electrode such as carbon cloth or graphite felt.

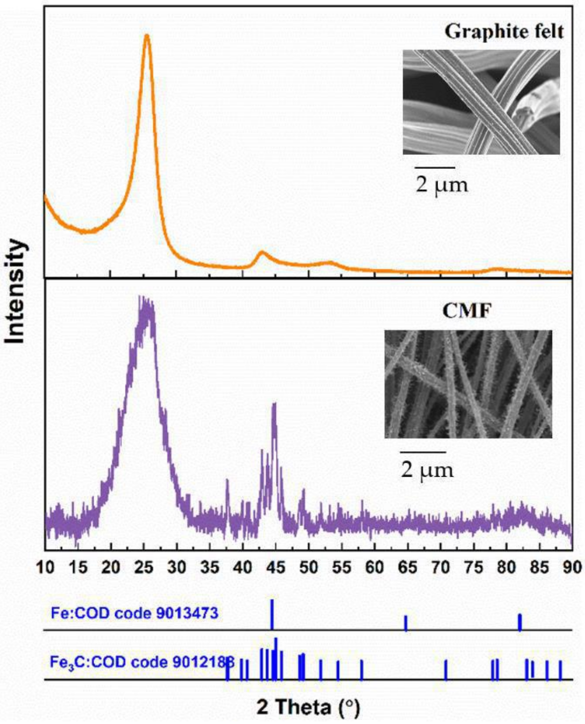


Fig. 2. XRD image of graphite felt compared with that of CCL (respective SEM images are given in the inset). SEM image of CCL (referred to as CMF in the figure) shows typical hair-like structures that contain CNTs.

3.2. V/Mn Flow Battery

1 M vanadium sulphate in 5 M sulfuric acid was used as the catholyte while 1 M manganese carbonate was dissolved in 5 M sulfuric acid with 1 M titanium sulphate as the anolyte. The titanium salt is used to prevent an irreversible conversion of manganese ions to manganese dioxide precipitates that usually lower electrolyte capacity. Fig. 3(a) shows the power density curves for the V/Mn flow battery. The presence of CCL resulted in a 35% enhancement of the peak power density (for V/Mn RFB using only graphite felt electrodes the power density was just under 40 mW cm^{-2} while the counterpart using CCL along with felts gave a higher peak power density of about 60 mW cm^{-2}), which is a good comparative result. Electrolyte capacity also appears to show about 50% improvement when using CCLs (Fig. 3b). The observation of two voltage discharge plateaus is most due to likely vanadium crossover to the manganese half-cell. First plateau could be related with Mn(III) conversion to Mn(II) while the second plateau could be associated with V(V) reduction to V(IV). It is most likely that the presence of V and Ti ions simultaneously contribute to inhibit MnO_2 precipitate formation, thereby mitigating capacity fading.

The results shown in Fig. 3 indicate that CCL works very well as an electrode catalyst for both vanadium and manganese RFBs. Despite that, the KPI values are still very low when compared with the literature [15, 16] and this is because of the use of a non-optimized reactor that involved placing the CCL between the flow channels and the felt electrodes to prevent fluid flow blockages due to protruding graphite fibers. This, in addition to low compression of the electrodes also may have reduced the electrochemical surface area for electron transfer reactions to occur. If a commercially sourced Scribner flow cell was employed then the CCL could be successfully placed in between the felt and the membrane, which could enhance performances significantly as discussed in the subsequent section.

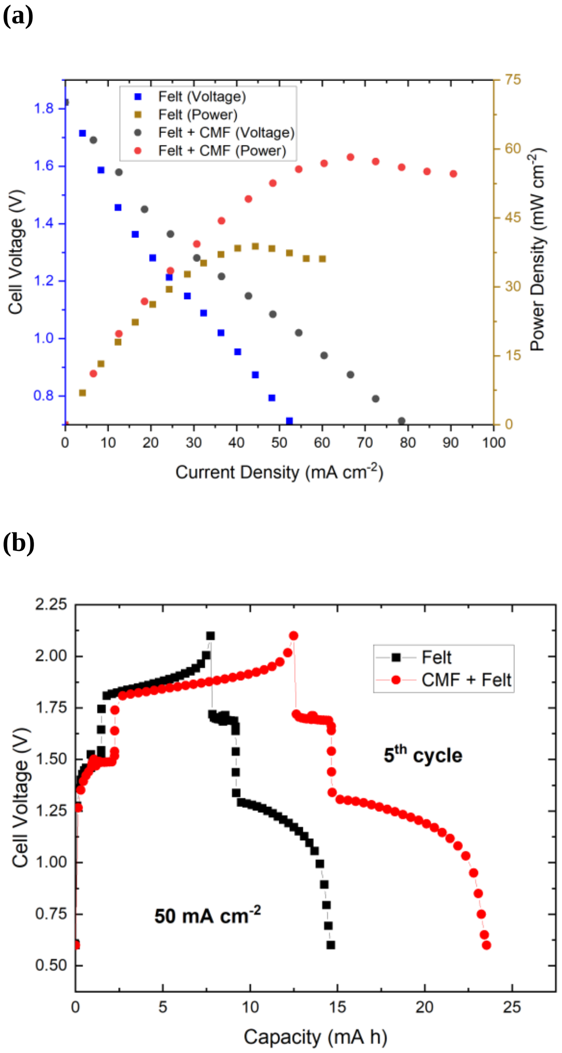


Fig. 3. (a) Polarization and power density curves for V/Mn RFB. (b) Cell capacity graph. System condition = 1 M $VOSO_4$ in 5 M H_2SO_4 for initial catholyte and 1 M $MnCO_3$ in 5 M H_2SO_4 with 1 M $TiOSO_4$ for initial anolyte, 50 ml min^{-1} flow, 100 ml volume (each), < 20% electrode compression (non-optimized), room temperature operation. CCL was placed in between the graphite felt and the flow channels in both half-cells.

3.3. System Integration of V/Mn Flow Battery

The purpose of this section is to consider the value of a vanadium/manganese redox flow battery (V/Mn RFB) as a potential commercially viable replacement for VRFBs owing to its lower costs associated with replacing vanadium electrolytes with more ubiquitous and therefore economical manganese-based electrolytes. This section therefore provides a brief qualitative consideration on how an optimized V/Mn RFB can be integrated effectively with the electric grid, renewable energy supply and/or water desalination plants. In this regard, Fig. 4 shows how the V/Mn RFB can be integrated with a solar PV or with wind turbines to provide support for a combined heat and gas powered (CHP) supply system. By means of a reversible solid oxide (RSO) cell, hydrogen, carbon monoxide and methane can be generated from excess renewable energy. Methanation reaction can also be performed inside the stack. However, 100% conversion cannot be achieved. The hydrogen may be stored or supplied directly to gas grids as shown in Fig. 4. In this manner, load levelling may be effectively achieved.

The RSO cell utilizes steam and carbon dioxide input streams that are generated from the CHP plant. The RSO cell produces carbon monoxide that can be applied as an input stream for a methanation unit, which can convert CO to methane or methanol. The latter can be implemented as a fuel or in fuel cells while the methane gas may be recycled to the CHP plant. The CHP may also be implemented for effective load balancing. The CHP system can use oxygen sweep gas generated by the RSO cell to optimize the combustion process and reduce other emissions. In this regard, the CHP is best employed for baseload power output rather than for peak load energy or electricity supply.

The CO_2 from the CHP exhaust gases may be captured and fed to the RSO cell, thus establishing the circularity of the carbon in the proposed configuration (Fig. 4). The H_2 can be input to the methanation process for hydrogenation of carbon monoxide (CO) to methane/methanol. Similarly, the thermal energy from the CHP may be employed for steam generation which could be used for H_2 production by the RSO cell. The V/Mn RFB can also act as a potential energy storage for a water desalination process. A typical water desalination plant needs energy intensive operation for high-pressure pumping of the saline water to the separation membrane assembly. Due to the significant amount of water to be pumped, this component requires considerable electricity input which could be supplied by renewable energy sources, like solar and wind.

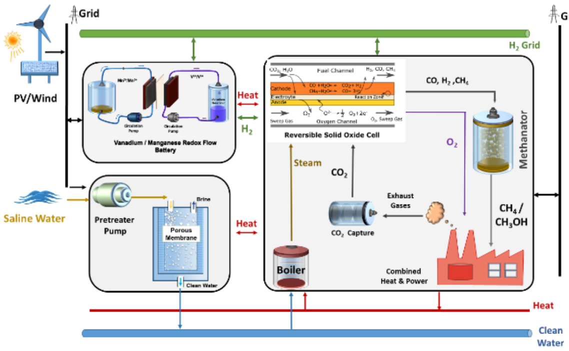


Fig. 4. Schematic depicting the proposed integration of the V/Mn RFB in a renewable energy powered integrated system for power, heat and gas generation and water desalination system. Adapted from a similar study reported by ACS on hydrogen/vanadium regenerative fuel cells [11].

Additionally, the excess electricity from renewable sources can be utilized by the RSO cell for H_2 generation, which may be stored for power generation when the renewable electricity is not available, thus facilitating continuous generation of electricity for the water desalination process.

4. Conclusion

This study shows the application of carbonized catalyst layers (homemade using electrospinning and carbonization) for improving performances for both VRFBs and V/Mn RFBs. The reactor used for these tests were also homemade, with limitations in non-optimized compression, fluid dynamics and other factors. Key performance indicators (KPIs) investigated in this work were limited to polarization curves and charge/discharge cycling efficiencies. The use of untreated graphite felts as control electrodes resulted in poor performances of both VRFB and V/Mn RFB systems but this was done deliberately to ascertain the effect of CCLs on KPIs. It was noted for VRFBs that peak power densities were about 40% higher when using CCLs, but energy efficiencies were not significantly improved (by approximately 15%) upon cycling. This is most likely because the CCL had to be placed in between the flow channels and felt electrodes to prevent graphite fibers from protruding into the flow fields and disturbing/blocking the fluid dynamics of the electrolytes. It is also hypothesized that the CCLs being brittle could have broken off during the cycling, possibly due to high initial overpotentials and uneven pressure exerted by the non-optimized reactor that could have broken some of the CCLs. Considering these results, the V/Mn RFB was not cycled much and the KPIs noted for peak power densities (35% improvement when using CCL in combination with graphite felt), and capacity utilization (50% higher when using CCL with graphite felt electrodes) suggest that further investigations with more robust versions of the CCLs could yield more optimized outputs, which could be considered for other redox couples for homemade and yet economical RFB reactors. Better KPIs leading to enhanced capacities and power outputs for V/Mn RFBs can lead to pilot scale testing by combining with renewable energy storage or water desalination plants for effective system integration investigations as further work.

Acknowledgement

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Significance of Electroactive Material Selection in Suspension Based Electrochemical Energy Storage Systems

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Due to their high energy density, extended cycling life, low self-discharge, high operating potential, lithium ion batteries (LIBs) are the preferred power source for many applications from portable devices to electric vehicles [1]. The initial step of manufacturing a LIB is typically preparation of suspensions, and those suspensions can be utilized directly (in flow based systems) [2] or in dried form (in solid state batteries) [3]. In either case, the performance of the resulting system is greatly influenced by the electrode/suspension microstructure. In the reported studies, several parameters such as mixing organization of components [4], solids loading [5] and particle characteristics (shape, size, size distribution etc.) [6] found influential on microstructure of the suspension and hence, the flow and electrochemical properties of the resultant electrode. The importance and necessity of using homogeneous suspensions comprised of dispersible (non-aggregated) electroactive particles in electrochemical energy storage systems was highlighted to obtain better electrochemical performance. In addition to this, it can be anticipated that the impact of utilizing aggregated particles will extend beyond electrochemical performance, where processability problems can be encountered due to instability and high viscous structure of the suspension. Thus, selecting the electroactive particle with suitable features and suspension microstructure design is very crucial to acquire suspensions with the low, i.e., affordable and operational viscosities and high electrical conductivities.

In the present study, to understand the variation in the suspension microstructure by virtue of used particle characteristics, two different electroactive materials, in aggregated and individual forms, were used to demonstrate the significance of the aggregation state of electroactive material on suspension characteristics. Rheological behavior and electrochemical impedance spectroscopy tests were carried out to comprehend microstructural evolution.

The results revealed that the rheological behavior of the suspensions could be improved almost one order of magnitude through utilization of dispersible electroactive particles. Moreover, higher solids fraction in the suspension achieved when these particles were used as they give chance to construction of higher energy dense storage systems.

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Investigating the Impact of Dip Coating on the Performance of Graphene Nanoplatelet-Coated Electrodes with Cellulose Binder for Organic Flow Batteries

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Organic flow batteries (OFBs) are a promising technology for large-scale and long-duration energy storage. They utilize organic compounds as the active material and are known for their high energy density, flexibility in design, and low cost. The unique characteristics of OFBs make them a highly promising technology for large-scale and long-duration energy storage, making them an area of active research and development. Unlike traditional batteries, OFBs offer customizable configurations, allowing for tailored solutions that can meet specific energy storage requirements. This adaptability extends to various sectors, such as renewable energy integration, grid stabilization, and off-grid applications.

Electrodes are important components of OFBs, and their performance affects the overall efficiency of the battery. Electrodes act as the interface where the electrochemical reactions take place, facilitating the flow of electrons and ions during charge and discharge cycles. The most common electrode used for OFB applications are graphite felts due to their high porosity and electrical conductivity properties. Various materials are currently under investigation to enhance the performance of graphite electrodes. Graphene, a two-dimensional carbon material, has emerged as a highly promising candidate since it exhibits exceptional electrical conductivity, mechanical strength, and chemical stability. Its unique structure and large surface area allow for efficient electron transfer and enhanced electrochemical reactions within the OFB system. Various binding agents or matrix materials are used for graphene-graphite binding in the literature. Polyvinyl alcohol (PVA), Polymethyl methacrylate (PMMA), and polymeric resins are some of the well-known binders used for this purpose. Cellulose is a natural polymer that also serves as an effective binder for graphene and graphite materials. Its remarkable compatibility with graphene and graphite makes it a commonly employed binding material. The inclusion of cellulose-based binders enhances the adhesion between the layers of graphene and graphite, resulting in improved mechanical strength and overall stability.

In this study, the performance of graphene-coated electrodes with cellulose as a binder for OFB applications was characterized. Pristine and 1- and 5-times dip-coated PAN-based carbon-felt electrodes were used as the electrode material. Different organic molecules were tested and TEMPO, (2,2,6,6-Tetramethylpiperidine-1-oxyl)-type air stable aminoxyl radical derivatives were used as the electroactive material. Electrochemical tests such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used to evaluate the electrochemical performance. Surface area analysis and characterization were performed using Brunauer-Emmett-Teller (BET) and scanning electron microscopy (SEM). According to the current literature, our work is the first study to investigate using cellulose as a binder for carbon-felt coating with graphene for OFBs. Figure 1 depicts the CV results of the pristine, 1- and 5-times dip-coated electrodes for a scan rate of 100 mV/s. The results show that with the increase in dipping times, the CV capacitance increased as well as all demonstrates the feasibility of using graphene-coated electrodes with cellulose binder for OFBs and the potential for improving their performance through multiple dip coatings.

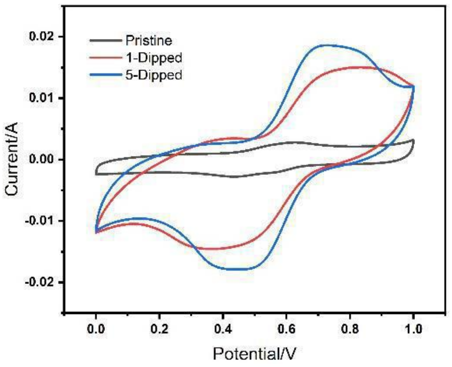

Figure 1. CV graph of pristine, 1- and 5-dipped graphite felts. Scan rate: 100 mV/s.

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SUPERCAPACITORS

Synthesis and characterization of nanocrystalline calcium hexaboride powders as a supercapacitor anode component

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Energy demand increases with the growing world population and the popularisation of portable electronics and electric vehicles that stimulates the development of energy storage devices such as batteries and supercapacitors from high power and energy density, which significantly relies on the research and development of advanced and unique materials. Supercapacitors (SCs) are energy storage devices commonly used in various applications that require an instantaneous power supply and fast response times. Therefore, obtaining high performance requires continuous development and modification of electrode materials. An ideal electrode for SC should exhibit high specific capacity and specific capacitance. The materials for efficient SCs should have good electronic and ionic conductivity and a high surface area with a porous structure. In recent years, a significant amount of research has been focused on improving supercapacitors' electrochemical performance by developing new anode materials. This study uses a low-cost solution-based process to synthesize Calcium Hexaboride powders as a supercapacitor anode material.

Calcium Hexaboride (CaB_6) is an alkaline earth metal boride with a high melting point (2235°C), high chemical stability, high hardness (27GPa), low density (2.45 g/cm^3) and high conductivity (bandwidth:0.8± 0.1 eV) [1]. Due to these properties, it has a wide range of applications such as anti-oxidant in the refractory industry, wear resistance structural ceramic and precursor in the production of boron nitride [2]. In this study, the synthesis, characterization and potential usage of CaB_6 powders as an anode component in energy storage applications were investigated. The properties (structural, physical and microstructure) of the synthesized powders were determined by XRD, FE-SEM and FTIR. The structural defect analysis was performed using the EPR technique. Electrochemical (CV, EIS, GCPL) measurements of the supercapacitor application of the powder were performed. 0.163 mA and 0.229 mA current ranges were obtained in the symmetrical device and in the asymmetrical device prepared with a graphite electrode, respectively. These results revealed that CaB_6 has potential as a new anode material for supercapacitor applications.

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NbB_2 as a promising electrode material for supercapacitors with high electrochemical performance

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The primary limitation in producing supercapacitors compared to batteries is their low energy densities. In recent years, big efforts have been made to increase energy densities to levels reached in batteries without losing their power densities. In the face of this challenge, the development of high-performance electrode materials is of significant importance [1,2]. As an electrode material, transition metal borides have been a possible choice for supercapacitors due to their excellent electrochemical properties, including high specific capacitance, great electrical conductivity, and good cycling loop retention [3]. They are also known for their strong chemical stability, abundance of electroactive sites, and shorter path lengths for ion diffusion. 2D boron-based materials such as Borophene and MBenes have also attracted attention as electrode materials in recent years [4,5].

In this work, the potential of NbB_2 which belongs to a group of transition metal borides as a novel, high-performance electrode material for supercapacitors, was investigated. NbB_2 powders were successfully prepared by a molten-salt assisted borothermal reduction method using Nb powder and amorphous B powder as starting materials at 850°C for 4h in N_2 atmosphere. Phase transformation was studied by XRD and morphology of materials was studied by SEM and TEM analysis. The results showed that NbB_2 was successfully synthesized in the presence of molten LiCl/KCl salts at lower temperatures and higher yields. When applied to a supercapacitor, the NbB_2 displayed a specific capacitance of 102 F/g at 1 A/g in the three-electrode system in 1 M Na_2SO_4 electrolyte. These findings indicate that NbB_2 has a strong potential as electrode material for supercapacitors.

Acknowledgements

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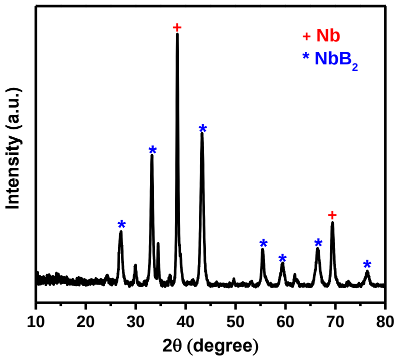

Fig. 1. XRD spectra of NbB_2.

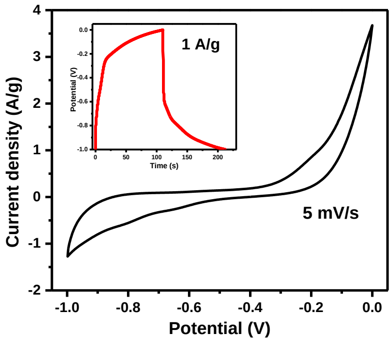

Fig. 2. CV and GCD (inset) curve of NbB_2.

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All-in-one Supercapacitors with high performance Asymmetric Configurations of Reduced Graphene-Quinoline Zinc Phthalocyanine Electrodes

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Phthalocyanines (Pcs) are macroheterocyclic compounds consisting of four isoindole units bonded to each other by nitrogen atoms at meso positions and can be obtained by changing the central metal ion and peripheral substituents and are used as pigments and have many applications such as energy conversion, gas sensor and liquid crystal. Quinoline is a heterocyclic aromatic organic compound that has various pharmacologically active synthetic and natural compounds of its derivatives are common [1]. The graphene family includes reduced graphene oxide (rGO), graphene oxide (GO), graphene sheets, and several-layer graphene members. GO has unique physical and chemical properties [2].

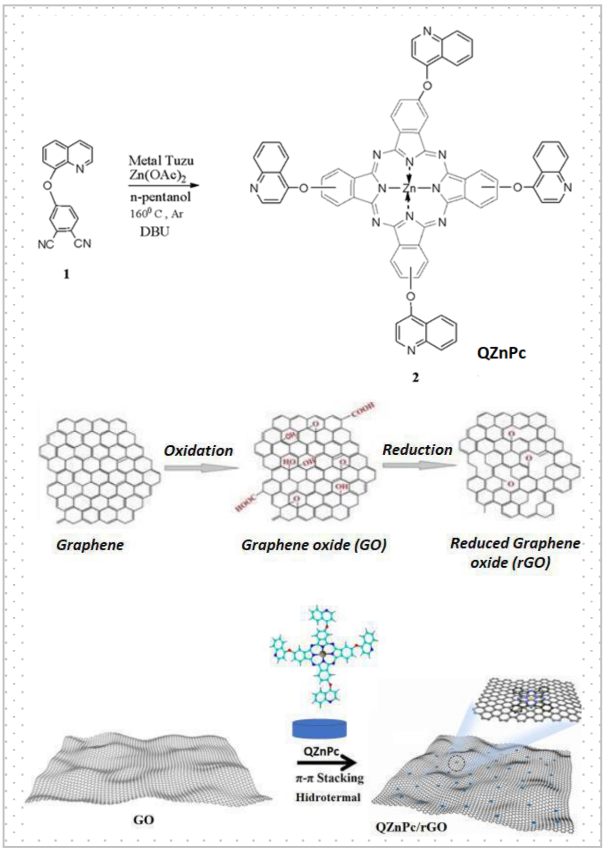

Figure 1. Schematic illustration of preparation for the QZnPc/rGO electrode

In this study, graphene oxide were obtained first, starting from graphite. Then, quinoline substituted phthalonitrile ligand was obtained. Qunoline zinc phthalocyanine (QZnPc), was obtained as a result of the reaction of this compound with metal salts under classical method conditions. The molecular structures of these newly synthesized substances were characterized by several spectroscopic methods. Later, new QZnPc/rGO nanohybrid material has been obtained as a result of the hydrothermal reduction reaction of GO with QZnPc we have also synthesized [3] (Fig. 1). Various methods were tried and their results were compared. Analysis and characterization of these obtained electroactive materials were made by methods such as FT-IR, BET, SEM, Raman, XRD, TGA. The results were successful as expected.

After the necessary characterizations are made, with this method, the electrode materials to be used in energy storage systems; CV, GCD and EIS electrochemical analysis techniques were applied to obtain information about supercapacitor performances and to examine its usability in the field of energy storage. This work provides a pathway to develop multi-functional composite structures with high storage capability to promote new technologies in scalable applications of new energy power generation systems.

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Biomass Derived High Porous Carbon via CO_2 Activation for Supercapacitor Electrodes

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The choice of the appropriate activation method, reagents, temperature and other parameters is a determining factor for obtaining high-quality, environmentally friendly and cost-effective porous carbons for use as an active electrode mass in energy storage systems. The chemical activation method using potassium hydroxide is the most effective and common method for producing activated carbon (AC) from biomass and is widely described in the literature. However, its use poses certain dangers to the environment and has technological drawbacks. KOH is a strong alkali and can cause serious irritation of the skin, eyes, respiratory tract, and other mucous parts of the body. Another drawback is the impact on the environment both during production and during disposal after use.

Alternative methods, such as physical activation using carbon dioxide (CO_2), can offer a safer, cheaper, faster, and more economical approach to the production AC from various biomass materials. Along with the advantages of the method, the study showed that CO_2 activation has some disadvantages. One of the main drawbacks is the lower high specific surface area (SSA) with a narrower range of pore sizes compared to the chemical activation methods. This observation could potentially be associated with the relatively low reactivity of CO_2 towards the oxidation of inorganic components in the raw material, particularly when compared to the efficacy of KOH. Therefore, there is a need to search for cheap and widely available biomass with the most suitable chemical composition and morphological characteristics for activation using CO_2. Based on a review of numerous experimental data, we have established that the use of biomass such as rice husk (RH) or walnut shell (WS), as raw material for the production of AC, is a comparatively reliable and effective choice for obtaining product with the best characteristics such as high SSA, developed porous structure, mechanical and chemical stability.

It was determined that the electrochemical characteristics of AC derived from RH and WSh, activated via KOH and through CO_2 are comprehensively different. Cyclic voltammetry (CV) curves acquired at 10 and 100 mV s^{-1} present a near-rectangular shape, indicative of electric double-layer capacitor behavior, with no peaks for Faradaic reactions observed. It was established that at a low scan rate of 10 mV s^{-1}, RH_KOH and RH_CO_2 reach high specific cell capacitances of 74.7 and 24.3 F g^{-1}. It is also noteworthy that at all scan rates between 5 and 500 mV s^{-1}, the cell capacitance of RH_KOH is significantly higher than that of RH_CO_2. In a general comparison of the RH and WSh, it is easily noticeable that the specific capacity of the for RH electrode activated with CO_2 is the lowest at all scanning speeds and charge-discharge currents, while the electrodes activated KOH exhibit the highest specific capacity. Contrary to rice husk, the characteristics of WSh activated with CO_2 do not lag significantly behind KOH.

We associate these features with the initial composition of the bio-precursors. For instance, the composition of rice husk contains an estimated 15-25% SiO_2 and other inorganic compounds, while the ash content in walnut shell averages 0.1-3.4%. Given that ¼ of the RH composition consists of inorganic components that are less susceptible to the effect of CO_2, the formation of new pores does not take place, ultimately leading to significantly lower SSA and electrochemical characteristics of RH_CO_2. In the sample treated with KOH, the ash and silicon present in the raw material are completely washed away, thereby increasing the total SSA and consequently improving the electrochemical characteristics of RH_KOH. Electrochemical impedance spectroscopy tests were conducted to investigate the resistive behavior of the materials. Similarly to RH, WSh samples exhibit nearly identical contact resistances (Rs ~ 0.36 Ohm). However, the charge transfer resistance of the electrode material derived from the CO2-activation process (Rct ~ 0.1 Ohm) is smaller than that derived from the KOH-activation process (Rct ~ 0.24 Ohm). Although both electrodes have dominant diffusion-controlled processes in the low-frequency region, ion diffusion is faster in WSh_CO_2_2h than in WSh_KOH (relaxation time is 1277ms).

In conclusion, the superior performance of the CO_2-activated material in comparison to the KOH-activated counterpart can be ascribed to key differences in their physicochemical properties. The hysteresis loop scanning analysis of the N_2 adsorption-desorption isotherms disclosed that CO_2 activation of resulted in a material with generally enhanced pore network connectivity.

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A temporal study of the ionic behavior during an electrical charge/discharge cycle in an electrolytic capacitor with carbone nanotubes

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Mathematical modeling and numerical simulations are widely used to understand ion migration in fields such as chemistry or energy storage. The model equations that describe ion migration in electrolytes can be derived from relatively simple principles while having complex forms. The theory used involves the Planck-Nernst equation [1]. Numerical simulations have confirmed the validity of the analytical expressions [2], and allow us to study in detail the behavior of ions in the electrolyte. Despite the complexity and non-linearity of ion behavior, we propose here a method to determine the temporal response of any Aluminum Electrolytic Capacitor (AEC). An operating model for a prototype is established by characterizing the dynamics of ionic charge transport under an electric field. Indeed, this work is based on the modeling, design and experimental characterization of a new energy storage system using carbon nanotubes. This model will have for the final objective to define the limits of operation and performances of the prototype.

AEC consists of two aluminum electrodes (anode and cathode), an oxide layer acting as a dielectric and an electrolyte. In AEC the electrolyte is used as conductor which can bring the negative potential closer to the dielectric via ionic transport. In order to characterize the electrolytic capacitors operating, the temporal evolution of the relaxation, resulting from the diffusion of the ions during the discharge of the electrolytic capacitor, is simulated. The model is a theoretical 1D model of an AEC. Two facing electrodes separated by an aluminum oxide dielectric with a thickness of 60 nm followed by 100 µm of the electrolyte are considered.

We studied the distribution of ion concentration, potential and electrical field in the electrolyte during transient regime. The analysis of the transient regime makes it possible to characterize the behavior of the ions subjected to strong electric field during the charge of the AEC. In order to analyze the temporal dynamics of the system, the simulation carries out a time study of 200 ns with a time step of 0.1 ns. Two phenomena are at play. First, the excitation phenomenon linked to the application of the potential and secondly the so-called relaxation phenomenon when no potential is applied. The total potential difference in the simulation has a "slot" type pulse shape. During the first nanosecond, the potential difference will vary from 0 V to 20 V in the system.

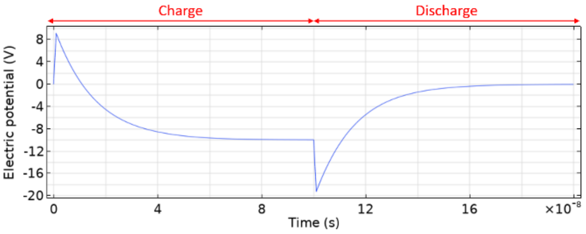

Figure 1 : Evolution of the electric potential at the interface between the dielectric and the electrolyte.

When a potential difference is applied between the two electrodes, the positive (and reciprocally negative) ions of the electrolyte will migrate towards the negative electrode (and reciprocally positive). However, due to the presence of the dielectric, the ions will accumulate at the dielectric-electrolyte boundary. As indicated by the Poisson equation [1], the accumulation of these electric charges will influence the electric potential at this point as depicted in **Error! Reference source not found.**.
In order to deduce the time constant of the evolution of the electric potential of the system, the temporal evolution of the electric potential during the charging and discharging of the capacitor is interpolated. In order to carry out this type of interpolation, algorithm based on the nonlinear least squares method is used. The latter was able to determine the coefficients allowing us to deduce the value of the time constant. A detailed study of these time constants is performed. A temporal characterization of the ionic behavior with respect to the applied potential difference gives information on the frequency response of the ionic conductor. This is an important point for many electronic components. Therefore, particular attention to the temporal characterization of these phenomena has been paid.

The present paper provides insights into the importance of the dynamics of ions in the electrolyte and their influence on the electric potential.

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Facile Synthesis of Cross-Linked Carbon Nanofiber Derived from PAN/Thiourea/Aluminum acetate as Supercapacitor Electrode

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Supercapacitors (SCs) have been considered promising devices in novel energy storage systems because of their high-power density and long life cycle life [1–3]. As a crucial part of SCs, the properties of electrode materials significantly affect the performance. To develop free-standing supercapacitor electrodes, cross-linked carbon nanofibers (CNFs) are good candidates for electrode materials. By using PAN, thiourea, and aluminum acetate as precursors were electrospun. The addition of thiourea and aluminum salt increased the surface characteristics and the conductivity of the CNFs by the decomposition of additives during thermal treatment. Carbon nanofibers were also synthesized for comparison from pure PAN and a solution of PAN/Thiourea. The results showed that the CNFs obtained from PAN, thiourea, and aluminum triacetate showed a good specific capacitance in alkaline aqueous electrolyte and it remained its rate capability at high current densities. The enhanced electrochemical performance is expected as a consequence of the synergistic effect of additives and cross-linked structure. The cross-linked structure promotes a fast transfer of electrons on the carbon nanofiber structure, which is conducive to charge storage. This method offers a new preparation approach for synthesizing high-performance CNFs with free-standing and cross-linked fibers.

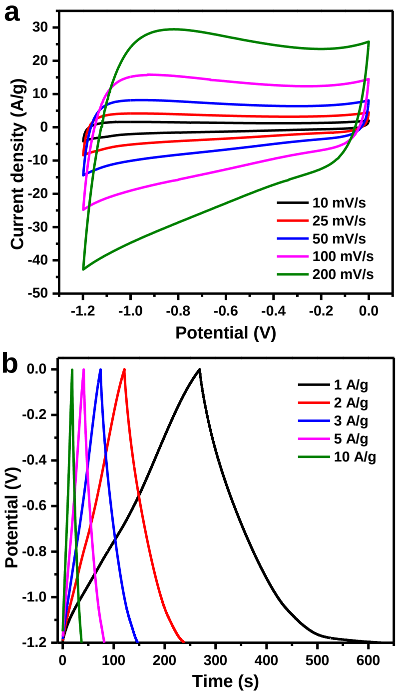

Figure 1. (a) CV curves at different scan rates and (b) GCD curves at different current densities.

Acknowledgements

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Recovery of Cobalt as CoS from Spent Li-ion Batteries and investigation of Supercapacitor performance of its composite with Cl-doped Graphene Oxide

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Batteries are currently the most widely used electrical energy storage technology in commercial applications. One of these battery kinds, secondary batteries, is also known as a rechargeable battery. They can be recharged by running electricity through the cells, and they are reusable [1].

The main electroactive materials used in the cathodes of commercial lithium-ion batteries (LIBs) are lithium metal oxides, such as $LiCoO_2$ (LCO), $LiNiO_2$, $LiMn_2O_4$, Li (Ni-Co-Mn)O_2 alloys, and $LiMPO_4$ (M: Metal) type compounds [2].

Lithium cobalt oxide (LCO) is the first cathode to be commercialized [3]. In the recycling of LCO, Leaching can be performed by using acid solution like HNO_3. Additionally, using H_2O_2 during LCO leaching operations readily converts Co^{+3} ions to Co^{+2} ions [4]. A new approach to the recycling of LCO is the leaching of LCO and precipitation of cobalt in the solution as cobalt sulfide. Then it can be used as supercapacitor electrode material [5], [6].

Experimental procedure of this study includes crushing of spent battery, dismantle of Li-on cell (LCO), stripping of cathode material from membrane, leaching of cathode material, precipitating of CoS by using Na_2S source, producing of Cl-doped graphene oxide (Cl-GO), preparing of electrode material for coin cell type supercapacitor by mixing COS and Cl-GO with PVDF and lastly, electrochemical measurements of supercapacitor by Using cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) tests. Experimental flow chart is shown at (Fig 1).

Produced materials were characterized by using FE-SEM, XPS, FTIR, BET. Electrochemical performance of the coin cell type supercapacitors were characterized EIS, CV and GCD tests. The produced supercapacitor showed enhanced capacitive property and cycle life. This work also showed a successful application of reusing of spent li-on battery active materials as an active material of a new energy storage device. This study brought an effective use of limited source for greener world.

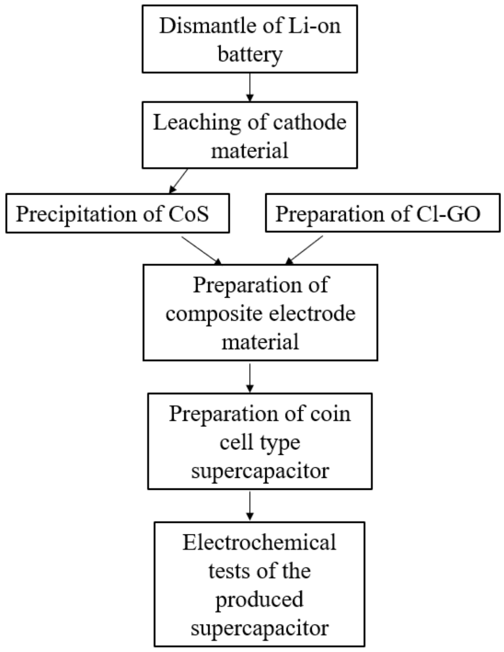

Figure 1. Experimental flow chart

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MXene-coated cotton fabrics for wearable supercapacitors

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Wearable electronics are expected to become more widespread in the future. Therefore, there is an increasing demand for low-cost, fast-produced and compatible energy storage devices. Supercapacitors differ from conventional capacitors due to their high charge storage capabilities. In addition, they contain a high specific surface area and a thinner electrolyte, thus, they can store hundreds of times more energy in seconds than conventional capacitors, and transfer the stored energy much faster than batteries [1].

High specific surface area of carbon-based materials provides an electrical double layer structure in nanometer sizes at the interface of the electrode and electrolyte molecules. However, these materials have disadvantages such as limited electrical conductivity, low mechanical properties and relatively shorter cycle life. MXenes show superior charge storage capability compared to other two-dimensional materials due to their high electrical conductivity (≈9800 S cm^{-1}), redox activity and volumetric capacitance (≈1500 F cm^{-3}) [2].

The current study investigates the electrochemical performance of $Ti_3C_2T_x$ (MXene) coated cotton fabrics for wearable supercapacitors. $Ti_3C_2T_x$, which has outstanding electrochemical performance and electrical properties, was used as electroactive material for coating process of cotton fabrics. $Ti_3C_2T_x$ was synthesized using Ti_3AlC_2 (MAX) phase according to middle intensive delamination method (MILD). Coating of cotton fabrics was carried out by spray coating using $Ti_3C_2T_x$ dispersions in different concentrations (1, 5 and 10 mg/ml). In this study, X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) were used for the characterization of MXene and MXene-coated fabric electrodes. The interaction between MXene and cotton surface was investigated by means of Scanning Electron Microscopy (SEM). Electrocehmical performance of MXene-coated fabric electrodes was investigated via electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) tests.

EIS tests were performed using three-electrode configuration in 1 M Na_2SO_4 aqueous electrolyte. Figure 1. shows the Nyquist plot of MXene-coated fabric electrodes in three different concentrations (1, 5 and 10 mg/ml).

The high slope in low frequency region is obvious for all fabric electrodes which is an indication of low ion diffiusion resistance of the electrodes. In addition, relatively similar semi circle of three electrodes show that electrodes have low charge transfer resistance which is advantageous for high electrochemical performance.

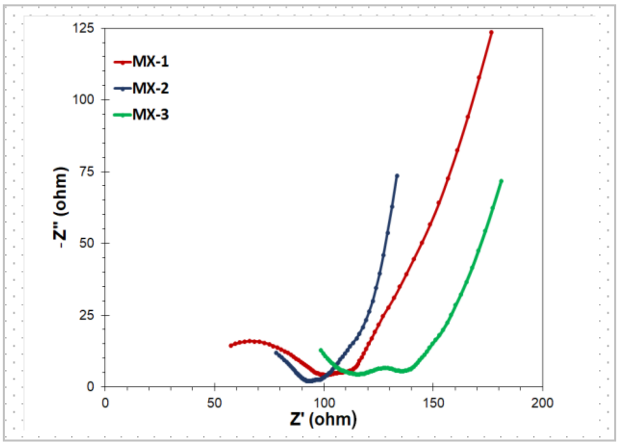

Figure 1. Nyquist plots of MXene-coated cotton fabric electrodes for 1 mg/ml (MX-1), 5 mg/ml (MX-2) and 10 mg/ml (MX-3).

This study provides an important contribution to the studies related to the rapid and facile production of wearable electronics, which will take place in our daily lives more in the future.

Acknowledgements

Authors acknowledge support from the Scientific Research Projects Coordination Unit of Bursa Technical University (Project Number: 221N025).

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Understanding the Solvent Effect in Slit-pore Supercapacitor Models using Molecular Modelling

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Supercapacitors have gained increased attention in recent years owing to their high-power density, charge efficiency, and long cycle lifetimes. The performance of supercapacitors has been improving through discovery of novel materials and the understanding of charging/discharging mechanisms [1]. Carbon-based materials have been widely studied as electrodes due to their good electrical conductivity, high surface area, and porosity control [2][3]. Ionic liquids are promising electrolytes with their high energy density and wide electrochemical window. However, their slow transportation properties and low electrical conductivity are drawbacks as pure electrolyte materials. Organic solvents are widely used to increase their conductivity and power density [1]. Molecular dynamic simulations allow to study charging dynamics and structure of supercapacitors with various properties in molecular level.

In this study, molecular dynamic simulations are conducted on supercapacitor systems consisting of carbon electrode, organic solvent acetonitrile (ACN) and ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF6). The electrodes are modelled as slit pores with 3-layers of honeycomb lattice model graphene sheets. System model is shown in Figure 1. The systems are built with pore width of 7.78 Å, 11.12 Å and 14.75 Å, ion fractions of 0.77 and 1.00, and solvent dipole moments of 2.06 D, 4.12 D and 6.12 D.

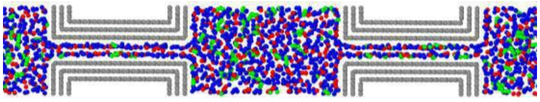

Figure 1. Simulated system. ACN (green), [$BMIM^+$] (blue), [$PF6^-$] (red)

Initial configurations are obtained with Packmol [4] and molecular dynamic simulations are conducted using the LAMMPS package [5]. Equilibrium simulations are followed by constant potential simulations with potential difference of 1.0 V. Systems are charged for 15 ns. The charging dynamics of the electrodes, kinetic properties, and molecular structure of the electrolyte at the interface and inside the pores are analyzed to understand solvent effect in slit-pore supercapacitor models. The charging profile of the electrodes, radial distribution functions, number and charge density of the electrolyte, diffusion coefficient, and ionic conductivity are calculated to explain the effect of system parameters on the supercapacitor models. Charging of the electrodes shows that presence of solvent increases the electrode charging under constant potential.

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Marine mucilage-based SiO_2/C nanocomposite for supercapacitors: transforming untapped bioresources into value-added products

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Sustainable electrode materials are often made from agricultural feedstock. Alternative biomass sources include micro- and macroalgae found in the marine environment. These organisms have a high growth rate and do not require agricultural land, freshwater or human activity. In recent years, temperature anomalies caused by climate change have led to harmful but nontoxic marine events, including mucilage outbreaks and algal blooms. Considering the huge amount of biowaste generated by such natural phenomena, turning this untapped resource into value-added products can yield remarkable environmental and economic benefits. Moreover, marine mucilage undergoes a self-activation process due to the abundance of natural seawater salts in its structure, avoiding the cost and environmental impact of an additional activation process.

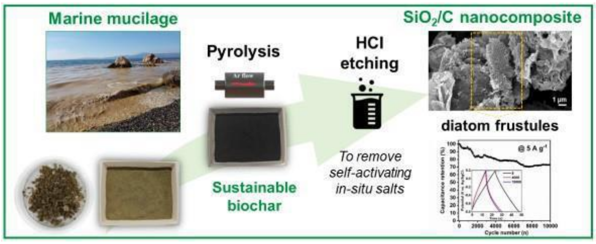

Figure 1. Synthetic process of SiO_2/C nanocomposite.

Diatoms, with their unique biosilica (SiO_2) cell walls known as frustules, are major marine organisms suspected to be involved in mucilage outbreaks. Despite being electrochemically inactive and non-conductive, SiO_2 contributes to the electrical double layer capacitance by its inherent surface potential, resulting in a very high differential capacitance of 180 μF cm^{-2} [1], exceeding the typical double-layer capacitance of carbon electrodes (10–20 μF cm^{-2}). Consequently, in recent years, efforts have been focused on employing inexpensive and environmentally benign SiO_2 for energy-storage applications.

Here, the marine mucilage (collected from the Marmara Sea, Turkey) was converted to SiO_2/Carbon composite via pyrolysis and acid etching (Figure 1) [2]. The composite exhibited a capacitance of 210 F g^{-1} at 0.5 A g^{-1} in 1M Na_2SO_4. The porous silica skeleton enhanced capacitance by enlarging the electrode/electrolyte interface, while the hierarchically connected pores ensured high electrochemical stability. The SiO_2/Carbon exhibited outstanding long-term cycling stability, retaining 70% of its capacitance after 10,000 cycles at 5 A g^{-1}.

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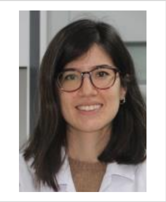

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Electrospun Activated Carbon (AC) and Polyacrylonitrile (PAN) Nanofibers for Supercapacitor Electrodes

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Activated carbon electrospun nanofibers have attracted much attention as supercapacitor electrodes due to their low cost and large-scale synthesis as well as their good mechanical properties [1-3]. Such nanofibers have been used as the supporting backbone for various pseudo-capacitive materials leading to the enhancement of the specific capacitance.

This research highlights the study of electrochemical properties of activated carbon (AC) nanofibers made together with different percentages of polyacrylonitrile (PAN) polymers (5, 10, and 15%) prepared by electrospinning techniques. The best C_s value was obtained from 15%AC of AC-PAN nanofibers.

Different scan rates were applied to 15%AC-PAN electrode nanofibers in the interval of 5, 20, 50 100, and 250 $\text{mVsec}^{-1,}$ and the best C_s value was obtained from 100 mVsec^{-1} with 63.76 Fg^{-1}. Then, long-term charge-discharge measurements were applied with a 100 mVsec-1 up to 200 cycles and C_s value reached to 158.33 Fg^{-1}. We had achieved a 40% increment, and this shows that if we proceed with this for long-term measurement up to 1000 cycles, we can achieve a much better result: a higher C_s value. In conclusion, this shows that this is promising nanofiber material for energy storage.

Table 1. Table of C_s value of 15%AC-PAN nanofiber electrodes at different scan rates.

Scan rate/ mVsec^{-1}	**C_s/ Fg^{-1}**
5	15.76135352
20	12.59127337
50	0.224933215
100	63.75779163
250	11.21460374

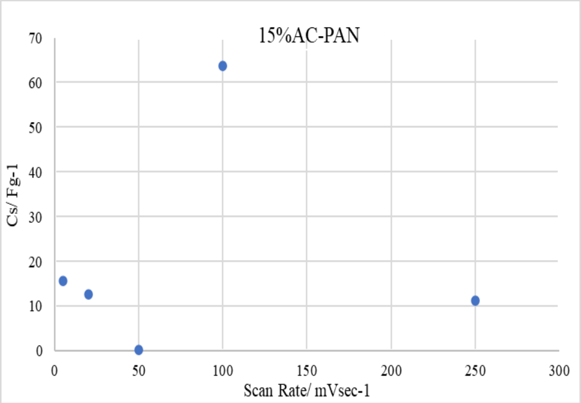

Figure 1. The C_s value plot of 15%AC-PAN nanofiber electrodes at different scan rates.

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Electrochemical Properties of Polytetrafluoroethylene (PTFE) Encapsulated in Polyvinylalcohol (PVA) Nanofibers and Their Supercapacitor Application

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Polytetrafluoroethylene (PTFE) nanofibers had received much attention due to their wide range of applications including in tissue engineering, drug delivery, cancer diagnosis, energy storage systems, optical sensors, along with water and air filtration [1-2]. Many different polymers have been mixed with PTFE to take advantage of its high resistance to chemicals and moisture, non-flammability, and non-stickiness. Yet, with a slippery surface, it does not stick and removes external factors easily [3].

This work investigates the effect of different combinations of polymers with PTFE for nanofiber materials to be applied as electrodes in supercapacitors application. The prepared materials using the optimized condition produced smooth scaffolds nanofibers between 55-200 nm range of sizes.

The best C_{sp} value was obtained from a mixture of PTFE-PVA. Different scan rates were applied to the sample in the interval of 5, 20, 50 100, and 250 $mVsec^{-1}$. The best C_s value was obtained from 100 $mVsec^{-1}$ as 202.45 Fg^{-1}. Then, long-term charge-discharge measurements were applied with a 100 $mVsec^{-1}$ up to 200 cycles and C_s value remain the same (no percentage enhancement between the first and last cycle). This shows that the stability of the developed supercapacitor is acceptable up to 200 cycles. However, the C_s value of this sample is higher than 200 C_s and it is comparable with reported electrodes in the literature, therefore, the PTFE-PVA combination has the potential as energy storage material.

Table 1. Table of C_s value of PTFE-PVA nanofibers at different scan rates.

Scan rate/ $mVsec^{-1}$	**C_s/ Fg^{-1}**
5	3.555654497
20	2.778272484
50	6.300089047
100	202.4487979
250	41.58504007

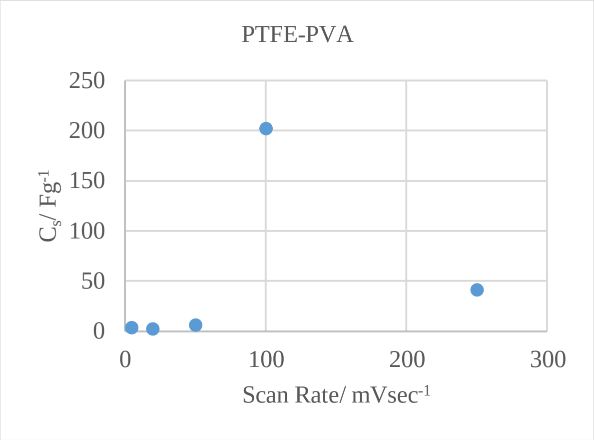

Figure 1. The C_s value plot of PTFE-PVA nanofibers at different scan rates.

Acknowledgements

The authors are grateful to the Scientific and Technological Research Council of Turkey (TUBITAK) (grant no. 221M075) for financial support. S. N. Abdul Halim would like to thank to TUBITAK 2221-Fellowships for Visiting Scientists and Scientists on Sabbatical Leave Support Program.

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Electrospun Cellulose Acetate (CA) and Polyvinylidene Fluoride (PVDF) Nanofibers for Supercapacitor Applications

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Sustainable biomass has drawn great consideration in developing green renewable energy storage devices with low-cost, flexible, and lightweight properties. Therefore, cellulose has been counted as a candidate to meet the needs of sustainable energy storage devices due to its most abundant nature, renewability, hydrophilicity, and biodegradability. Particularly, cellulose-derived nanostructures (CNS) are more promising due to their low-density, high surface area, high aspect ratio, and excellent mechanical properties [1-2].

This research highlights the electrochemical properties of electrospun cellulose acetate (CA) and polyvinylidene fluoride (PVDF) nanofibers.

Different scan rates were applied to the sample in the interval of 5, 20, 50 100, and 250 mVsec$^{-1,}$ and the best C_s value was obtained from 100 mVsec^{-1} with 89.00 Fg^{-1}. Then, long-term charge-discharge measurements were applied with a 100 mVsec^{-1} up to 200 cycles and C_s value reached to 96.08 Fg^{-1}. We achieved 0.92% increment, and this shows that if we proceed with this for long-term measurement up to 1000 cycles, we can achieve a much better result: a higher C_s value. In conclusion, this shows that this is promising nanofiber material for energy storage.

Table 1. Table of C_s value of cellulose acetate (CA) and polyvinylidene fluoride (PVDF) nanofiber electrode at different scan rates.

Scan rate/ mVsec^{-1}	C_s/ Fg^{-1}
5	13.21460374
20	12.91184328
50	2.787177204
100	89.00267142
250	19.16295637

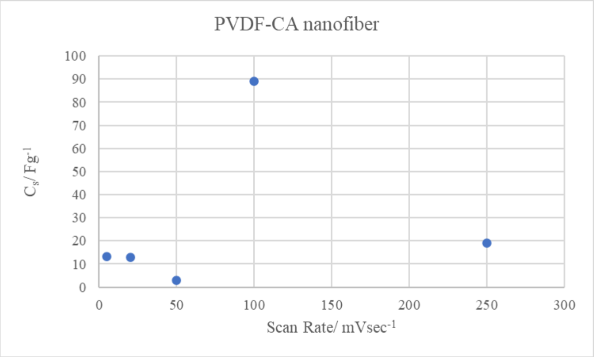

Figure 1. The C_s value plot of cellulose acetate (CA) and polyvinylidene fluoride (PVDF) nanofiber electrode at different scan rates.

Acknowledgements

The authors are grateful to the Scientific and Technological Research Council of Turkey (TUBITAK) (grant no. 221M075) for financial support. S. N. Abdul Halim would like to thank to TUBITAK 2221-Fellowships for Visiting Scientists and Scientists on Sabbatical Leave Support Program.

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Electrospun Silicon Dioxide (SiO_2) and Polyvinylidene Fluoride (PVDF) Nanofibers for Supercapacitor Electrodes

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Silicon dioxide (SiO_2) has recently drew huge research interest as the electrode materials for supercapacitor due to ease fabrication and integration possibility [1]. On top of that, research had confirmed that SiO_2-containing supercapacitor offers high cycle stability and able to facilitate ion transfer by generating a structure with active sites [2].

This research highlights the study of electrochemical properties of 15% SiO_2-containing nanofibers made together with of polyvinylidene fluoride (PVDF) polymer prepared by electrospinning techniques.

Different scan rates were applied to 15% SiO_2-PVDF nanofiber electrode in the interval of 5, 20, 50 100 and 250 $mVsec^{-1}$ and the best C_s value was obtained from 100 $mVsec^{-1}$ with 39.54 Fg^{-1}. Then, long term charge-discharge measurements were applied with a 100 mVsec-1 up to 200 cycle and C_s value reached to 126.67 Fg^{-1}. We had achieved 220% increment, and this shows that if we proceed this for long term measurement up to 1000 cycle, we can achieve much better result: a higher C_s value. In conclusion, this shows that this is promising nanofiber material for energy storage.

Table 1. Table of C_s value of 15% SiO_2-PVDF nanofiber electrode at different scan rates.

Scan rate/ $mVsec^{-1}$	**C_s/ Fg^{-1}**
5	9.661620659
20	34.26090828
50	11.23775601
100	39.53695459
250	8.194122885

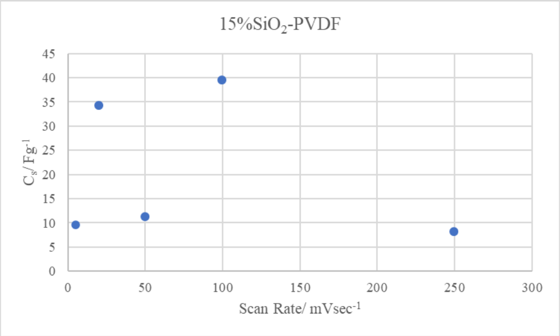

Figure 1. The C_s value plot of 15% SiO_2-PVDF nanofiber electrode at different scan rates.

Acknowledgements

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Electrochemical Properties of Electrospun Metal-Organic Frameworks (MOFs) Nanofibers as New Hybrid Electrode Materials for Supercapacitor Applications

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A wide range of promising functional metal–organic frameworks (MOFs) nanofibers have been reported to date, and their potential use in various technological fields has been investigated [1-3].

This research highlights the study of electrochemical properties of polyvinylidene fluoride (PVDF) nanofibers made together with different percentages of UiO-66 (Zr-terephtalic acid MOF) and MOF-199 (Cu-trimesic acid MOF) metal-organic frameworks materials (5, 10 and 15%) prepared by electrospinning techniques. The best Csp value was obtained from 15% UiO-66 and MOF-199 MOF-PVDF nanofibers.

Different scan rates were applied to 15% percentage of both samples; UiO-66-PVDF and MOF-199-PVDF nanofiber electrodes in the interval of 5, 20, 50 100, and 250 mVsec^{-1} and the best C_s value was obtained from 100 mVsec^{-1} with 221.10 and 358.33 Fg^{-1} respectively. Then, long-term charge-discharge measurements were applied with a 100 mVsec^{-1} up to 200 cycles and C_s value reached to 358.77 and 534.28 Fg^{-1} respectively.

We had achieved 62% and 49% increments from both MOFs-PVDF nanofibers, and this shows that if we proceed with this for long-term measurement up to 1000 cycles, we can achieve a much better result: a higher C_s value. In conclusion, this shows that this is promising nanofiber electrode material for supercapacitor application.

Table 1. Table of C_s value of 15% MOFs-PVDF nanofibers at different scan rates.

Scan rate/ mVsec^{-1}	**C_s/ Fg^{-1}**	
	15% UiO66-PVDF	15% MOF199-PVDF
5	3.555654497	55.50311665
20	2.778272484	5.075690116
50	6.300089047	1.029385574
100	202.4487979	358.3259127
250	41.58504007	60.60552093

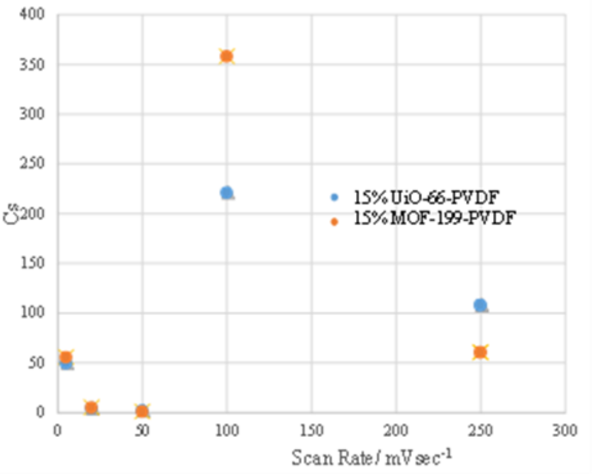

Figure 1. The C_s value plot of 15% MOFs-PVDF nanofibers at different scan rates.

Acknowledgements

The authors are grateful to the Scientific and Technological Research Council of Turkey (TUBITAK) (grant no. 221M075) for financial support. S. N. Abdul Halim would like to thank to TUBITAK 2221-Fellowships for Visiting Scientists and Scientists on Sabbatical Leave Support Program.

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Development of Metal Organic Framework Modified Carbon Paste Electrode for Supercapacitor Applications

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Metal–organic framework (MOF) is a comparatively novel group of attractive materials for specific electrochemical sensing because of its electrocatalytic activity and large surface area. [1]. They have been combined with carbon paste electrodes (CPE) for electrochemical studies and electroanalysis, however, their applications in energy storage devices are limited and not widely reported [2].

Therefore, our research focus on modified CPE in combination with MOFs; UiO-66 and MOF-199. The UiO-66/CPE electrode was prepared by mixing 80% graphite powder with 20% mineral oil and 15% of UiO-66 and MOF-199/CPE electrode was prepared by mixing 80% graphite powder with 20% mineral oil and 5% MOF-199 respectively. As a result; two nanostructure-modified electrodes were obtained.

Different scan rates were applied to both nanostructure-modified electrodes; in the interval of 5, 20, 50 100, and 250 mVsec$^{-1,}$ and the best C_s value was obtained from 100 mVsec^{-1} with 47.5 and 104.1 Fg^{-1} respectively. Then, long-term charge-discharge measurements were applied with a 100 mVsec^{-1} up to 200 cycles and C_s value reached 69.4 and 48.3 Fg^{-1} respectively. We conclude that MOFs composites seem to be the best electrodes for supercapacitor applications.

Table 1. Table of C_s value of MOFs/CPE electrodes at different scan rates.

Scan rate/ mVsec^{-1}	**C_s/ Fg^{-1}**	
	UiO66/CPE	MOF199/CPE
5	7.824	25.46
20	7.355	19.5
50	14.9	37.18
100	47.5	104.1
250	9.12	18.92

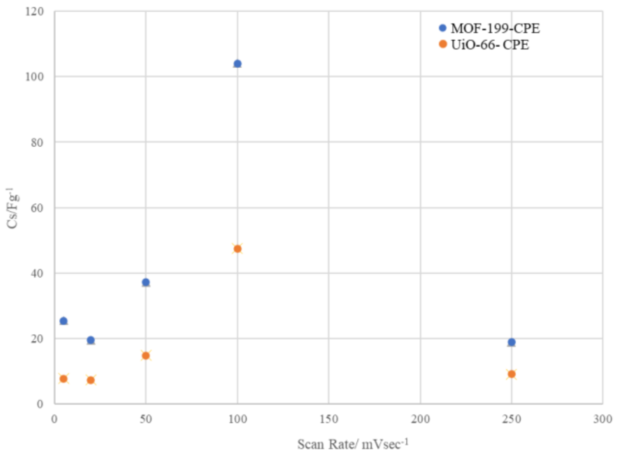

Figure 1. The plot of C_s value of MOFs/CPE electrodes at different scan rates.

Acknowledgments

The authors are grateful to the Scientific and Technological Research Council of Turkey (TUBITAK) (grant no. 221M075) for financial support. S. N. Abdul Halim would like to thanks to TUBITAK 2221-Fellowships for Visiting Scientists and Scientists on Sabbatical Leave Support Program.

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Synthesis and Characterization of MoB Electrode Material for Electrochemical Energy Storage

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Supercapacitors have emerged as promising energy storage devices due to their high power density, rapid charge-discharge capabilities, and long cycle life [1,2]. To further improve their performance, extensive research has focused on developing new electrode materials. Recently, metal borides have gained considerable attention as potential electrode materials for supercapacitors due to their unique properties, such as high electrical conductivity, excellent chemical stability, and large specific surface area [3].

Several synthesis methods of inorganic nanomaterials include sol-gel, combustion, hydrothermal, solvothermal, sonochemical, coprecipitation, and molten salt, etc. Among these methods, the molten salt method has emerged as a powerful, eco-friendly alternative for the synthesis of metal borides. The major advantages of molten salt method are low costs, low vapor pressures, high thermal stabilities, non-toxicity, and non-flammability [4,5].

This study aimed to explore the potential of MoB, a type of transition metal boride, as a new and high-performance electrode material for supercapacitors. The synthesis of MoB powders was accomplished using a borothermal process with the assistance of molten salt. The starting materials included Mo powder and amorphous B powder. The synthesis process was carried out under specific conditions: a temperature of 850°C, a duration of 4 hours, and an N_2 atmosphere. The phase transformation of the materials was assessed using X-ray diffraction (XRD), while scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were employed to examine the morphology of the materials. The tests of electrochemical performance of MoB electrode in 1 M $NaSO_3$ electrolyte revealed that MoB has a strong potential as electrode material for supercapacitors.

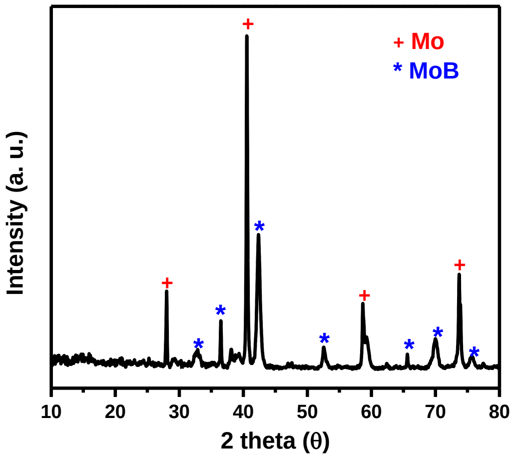

Fig. 1. XRD spectra of MoB.

Acknowledgements

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Investigation of various aqueous electrolytes on the electrochemical characteristics of supercapacitors based on activated carbon

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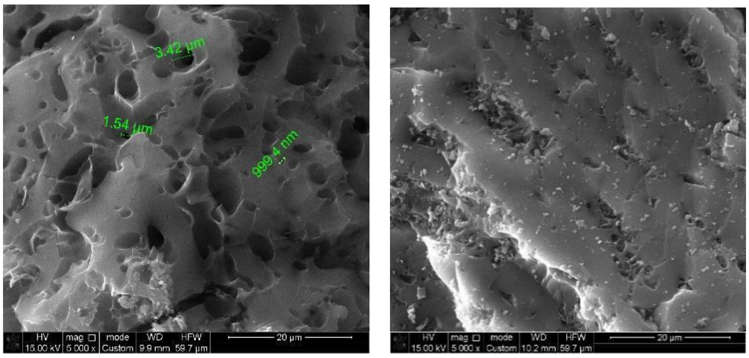
Supercapacitors (SCs), also known as electrochemical capacitors (ECs), are recognized as a major device for energy storage and are also attracting increasing interest due to their continuous practical use in mobile electronic devices, electric vehicles and fuel cells [1,2]. SCs also include pseudocapacitors and electrical double layer capacitors (EDLCs). In particular, EDLCs have a physical charge accumulation mechanism that creates an electrical double layer (EDL) on the surfaces of both electrodes [3].

Electrolytes play a vital role, and there are two forms of electrolytes: aqueous electrolytes and organic electrolytes. Aqueous electrolytes have obvious advantages over organic electrolytes, such as high conductivity, high safety and low cost. In addition, compared to organic electrolytes, aqueous electrolytes have a resistivity that is at least 20 times lower than that of organic electrolytes, which means that the power density of a supercapacitor using aqueous electrolytes is very high. In addition, the ionic conductivity and electrochemical potential window of the electrolytes also affect the efficiency of SCs [4]. In this study, the advantages of aqueous electrolytes prompted us to use and compare such as electrolytes 6M KOH, 1M Li_2SO_4 and 1 M Li_2SO_4 + 0.5 M KI. For preparation of composite electrodes, we used synthesized carbon material based on walnut shells and commercial carbon of Cabot Norit Nederand B.V. (producer Netherlands) (mass 85%) with addition of PVDF, "Kynar HSV900" (mass 10%) as binder and acetylene carbon black (mass 5%), "C-65, Timcal C-NERGY Imerys" as conductive additive.

Various characterization tools such as SEM/EDX, BET and X-ray Diffraction Analysis, Thermogravimetry (TG/DTA), and Raman spectroscopy were used to evaluate the carbon materials. The electron microscopic images shown in Figure 1 show the openwork morphology typical of activated carbon (AC) based walnut shells and internal porosity.

Electrochemical tests were performed using an Elins P-45X multi-channel potentiostat-galvanostat instrument. The obtained activated carbon electrodes were used as supercapacitor electrodes using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) techniques in aqueous electrolytes. In the potential range from 0 to 1 V, CV measurements were recorded at various scanning speeds ranging from 20 to 160 mV/s. GCD was performed at specific currents of 100, 500, 1000, and 2000 mA/g with a voltage range of 0 to 1 V. EIS measurements were evaluated in the frequency range (0.01 Hz to 100 kHz) at a sine potential amplitude of 10 mV.



1 2

Figure 1. Scanning electron microscopy images of porous carbon materials (1-walnut shells and 2-commercial carbon).

Synthesized carbon material based on walnut shells calculated capacitance values of 266 F/g for 1 mol/L Li_2SO_4 and 273 F/g for 6 mol/L KOH, respectively. Evaluation of the electrochemical characteristics showed that the porous walnut shell-derived carbons were characterized by outstanding charge propagation and gravimetric capacitance comparable or even much higher than that of commercially available AC.

Acknowledgements

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Rational design of iron nitride/carbon cloth electrode as an anode for asymmetric supercapacitors

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It is essential to develop novel materials for batteries and supercapacitors in order to boost the effectiveness of energy storage systems and ease the switch from non-renewable to green and sustainable energy sources. Among them, asymmetric electrochemical capacitors and hybrid capacitors are strongly investigated to meet current performance expectations [1]. However, the device's electrochemical performance is directly correlated with the morphology and structural characteristics of the electrode material. Electrochemical capacitors can be divided into two distinct groups: electric double-layer capacitors (EDLC) and pseudocapacitors, of which the former consist of redox-active electrode materials like transition metal-based (Fe, Mn, Ru, Co) oxides, hydroxides, sulfides, or nitrides [2,3]. Iron compounds, including oxides and nitrides, are among the different materials utilized for negative electrodes and are regarded as a viable choice because of their electrochemical performance, wide working potential window, low cost, and natural abundance [4].

In this study, we investigated environmentally friendly synthesis protocol for iron oxide/carbon cloth (Fe_2O_3@CC) composite electrodes. Iron oxide was used as the precursor for the formation of iron nitride and was electrochemically deposited on hydrophilic carbon fabric using a typical three-electrode setup at a constant potential of -1.4 V vs. Ag/AgCl and an electrolyte of 0.02 M $FeCl_3$. The conversion of iron oxide to iron nitride was performed using high temperature annealing in ammonia atmosphere.

According to the obtained results, iron nitride-carbon cloth electrodes exhibit battery-like behavior, showing both visible peaks at the desired potential and a clear plateau during galvanostatic charge and discharge experiments. Due to the increased electrical conductivity of the nitrides, flexible electrodes with deposited iron nitride demonstrated significantly greater capacity retention with increasing current loads compared to their iron oxide counterparts. XRD measurements revealed that electrochemical deposition protocol yields an amorphous inorganic phase, which can provide electroactive sites for redox reaction. Finally, the iron nitride-carbon cloth electrode was used as the anode of an asymmetric system, combined with an Mn-based cathode.

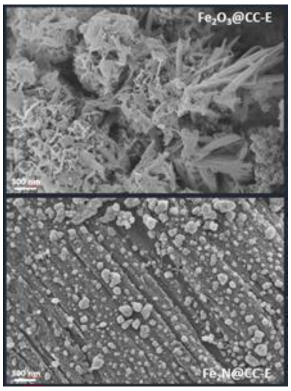

Figure 1. FESEM images presenting morphology of the flexible iron-based electrodes.

The findings show the possibility of flexible iron-based electrodes for use in supercapacitors or hybrid capacitor applications.

Acknowledgements

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RENEWABLE HYDROGEN/ FUELS

Transition metal nitrides in ammonia production: Challenges and Possible Solutions

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Protonic Ceramic electrochemical devices can have an important role in the decarbonation of industrial chemicals, in line with current European green directives that aim to reduce CO_2 emissions by the development of new C-neutral technologies for industries and processes[1].

The most common protonic ceramic electrolyte materials are those of alkaline earth doped cerates, zirconates and their solid solutions, due to their high proton conductivity and low activation energy. Typically these are materials of the perovskite structure, with the best perfoming containing basic A-site elements such as barium, e.g. $BaZrO_3$-$BaCeO_3$, with minor B-site acceptor doping by rare earth elements, such as Y,Gd.

The current presentation will discuss ongoing studies performed in the University of Aveiro, Portugal, that aim to eletrochemically synthesise NH_3 directly from H_2O and N_2, with the input of renewable electricity, by the use of such Proton Ceramic Electrolyser Cells (PCECs), using these electrolyte materials, Fig.1.

Ammonia (NH_3) is a key chemical that is produced as a precursor in a range of products that are vital to society, such as fertilizers and medicines. Nevertheless, the current Haber-Bosch process produces ammonia from nitrogen and hydrogen at high pressures (100-300bar) in the temperature range 300-550ºC [2,3], with a very high energy consumption, low equilibrium conversion (10-15%) and with the production of ~300 million metric tons of CO_2 per year due to its reliance on hydrogen produced from natural gas [2,3].

New green concepts for NH_3 production, are, therefore, urgently needed, such as that of Fig.1.

In our work we will highlight the possible use of oxynitride materials as electrocatalytically active electrodes for these devices, focusing on their potential advantages, as well as their limitations and key challenges for successful implementation..

Work will describe, the preparation of the oxy(nitride) materials, their stability, their compositional tailoring and their processing to form potential electrodes, Fig.2. This, includes the chemical compatiblity of the oxynitride materials and the aforementioned proton ceramic eletrolytes. Further discussion will assess how modification of the composition of the oxynitrides by control of synthesis conditions can effect their subsequent properties. From this basis, preliminary results of the performace of these materials as potential catalysts for NH_3 formation will be presented.

Figure 1. Schematic electrochemical NH_3 production using a PCEC.

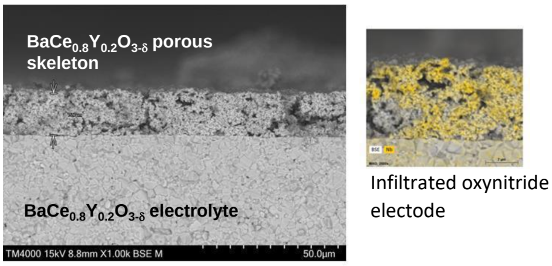

Figure 2. SEM micrographs of an oxynitride electrocatalyst deposited on a proton ceramic substrate.

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Photocatalytic CO_2 reduction

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As one of the major greenhouse gases, CO_2 emission has to be reduced for a sustainable world. While new and cleaner energy conversion technologies have been developed to cease the dependency to the fossil fuels, the effective technologies to convert the emitted CO_2 into more environmental friendly, and preferably economically valuable chemicals have been also investigated. Photoreduction of CO_2 using solar energy and water, as inspired by photosynthesis in plants, has been investigated extensively for this purpose in recent years. Figure 1 shows the increase in number of publications through years with the "photocatalytic CO_2 reduction" keyword in Web of Science (WOS) database [1]. When this technology becomes commercially available, it will be possible to produce valuable chemicals with a clean technology while reducing CO_2 emissions into the atmosphere.

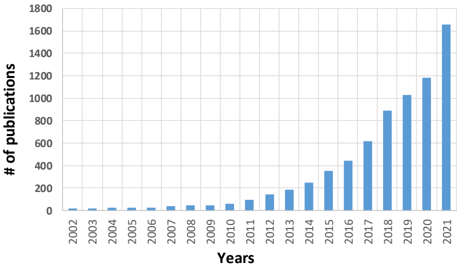

Figure 1. Publications on photocatalytic CO_2 reduction (based on WOS search in 13.4.2023 with the keyword of "photocatalytic CO_2 reduction" as *topic*)

The photoreduction of CO_2 can be carried out photoelectrochemically (using photoactive electrodes containing cocatalyst) or photocatalytically (using particulate photoactive semiconductors loaded by cocatalyst). Although the photoelectrochmical process has to be in liquid phase, the photocatalytic processes are performed in both liquid and gas phase conditions with different product distribution [2].

Photoreduction of CO_2 using solar energy is clearly quite appealing; however, there are several challenges to overcome for a successful commercialization of the process. For example, semiconductors with sufficient visible light activity are needed if the process is going to use solar irradiation; unfortunately, most of the available semiconductor are active under UV or have very low efficiency under visible light irradiation. Additionally, the semiconductor to be used should be cheap, stable and harmless to the human health and environment. Consequently, one of the main research direction in the field is to find new and better semiconductors by searching among natural materials, modifying existing semiconductors or synthesizing completely new materials. Indeed, from simple metal oxides to metal organic frameworks (MOFs) and halide perovskites, various materials have been studied for this purpose. Similarly, effective cocatalysts to improve the charge separation and reaction rate are also investigated.

Due to the complexities in the process and challenges in finding suitable semiconductors and cocatalysts, the experimental works has to be supported by computational tools to reduce the search space, and to direct the experimental studies to the most the promising conditions. Two classes of computational tools have been used for this purpose as in other similar research fields: molecular modeling (mostly DFT based) and machine learning. While the molecular modeling is used to determine the suitability of physical and chemical properties of the new materials, the machine learning allows for the screening of larger number of alternatives by predicting the properties or performance of completely new materials using information from already known alternatives. This two approach are often used together through computational material databases like Material Project, OQMD, AFLOWLIB, and Computational Material Repository containing physical and chemical properties of hundreds of thousands materials. Data from these databases, together with experimental data accumulated on the subject through the years, create a big opportunity to learn from the past experience via machine learning and use this information to discover, select or analyze materials with potential as semiconductor or cocatalyst.

To sum up, although significant challenges are still ahead for the successful commercialization of CO_2 photoreduction, there are also significant development to speed up the progress in the field.

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Bibliometric Analysis of Photocatalytic CO_2 Reduction

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The CO_2 concentration levels in the atmosphere have exceeded 400 ppm in March of 2014. That has been reported as a milestone with a 40% increase from the 1750s [1] and the global CO_2 concentration level will be expected to rise at around 2 ppm per year [2]. Therefore, the efforts to limit atmospheric CO_2 concentration have been gaining lots of interest from scientific and commercial communities. Whereas scientists are pioneering novel technologies and products, industrialists try to convert them to practical and economical applications. The investigation of the patterns in scientific and commercial works and the relationship between them may help assess future trends and provide new pathways for future scientific or commercial endeavors. To contribute to these efforts, a bibliometric analysis of photocatalytic CO_2 reduction was performed through scientific and commercial databases.

In the first step, the topic of photocatalytic CO_2 reduction was searched in the Web of Science core collection (WOS) database using "photocatalytic CO_2 reduction" and "photocatalytic carbon dioxide reduction" keywords; 9969 published papers were extracted from 1987 to 2022. Publications trends as well as the types of publication are presented in Fig. 1a. Research areas (32) were also extracted from these papers via author keywords, and the relationship between research areas and citation numbers was analyzed through the stage of photocatalytic CO_2 reduction (PCCO2R). Moreover, an analysis was also carried out on author keywords of all published papers to reveal the top 10 most commonly used materials, methods, modifications, concepts, and so on (Fig. 1b).

Then, the commercial trends in this area were sought by Google Patents for all patents (298 patents) from 2011 to 2022, and it was associated with scientific publications in terms of number of patents, country contributions, and research areas (Fig. 1c). In this bibliometric analysis, it was revealed that PCCO2R is at the early stage of its life cycle and an open to further investigations in both scientific and commercial level. In addition, the keyword analysis not only shows the top 10 most used materials, modifications, and so on for the PCCO2R application, but also demonstrates a possible candidate list.

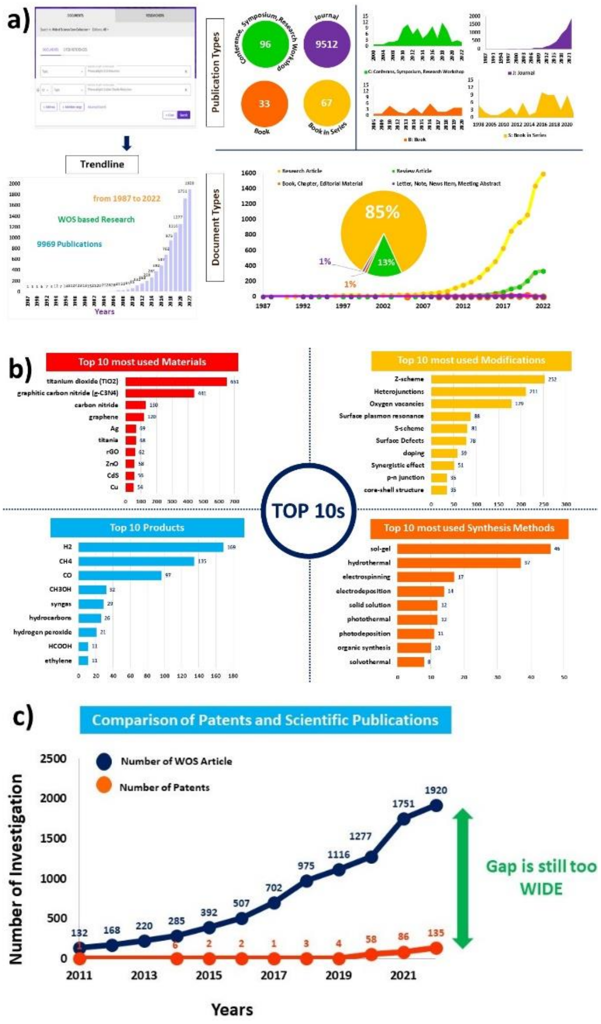

Figure 1. (a) Annual distributions of all published papers on WOS for the PCCO2 topic, (b) keyword analysis for the top 10 materials, modifications products, and synthesis methods (c) relations within the number of published papers and patents.

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Analysis of Data from Published Articles for Photocatalytic CO2 Reduction over Halide Perovskites

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Among all greenhouse gases accumulating in the atmosphere, carbon dioxide is the main reason of global warming[1]. Hence, extensive efforts have been made to develop environmentally friendly technologies that eliminate CO_2 emmisions. Photocatalytic CO_2 reduction, i.e. artificial photosynthesis, is one of the most promising strategies to convert the undesired CO_2 into valuable chemicals such as methane, methanol, carbon monoxide and hydrogen by means of solar energy[2]. In the search of an efficient photocatalyst, various semiconductors have been employed for CO_2 reduction processes; recently, halide perovskites have been explored as an appropriate candidate due to their tunable band gap, favorable light absorption capacity, and long carrier transport length as observed solar cell applications[3,4].

Halide perovskites are represented with a chemical structure of ABX_3, where A and B sites are cations and X is a halide anion[5]. The properties of halide perovskites photocatalysts can be tuned by composition engineering, doping or using co-catalysts. In this context, numerous experimental studies have been performed to design halide perovskite photocatalysts with excellent efficiency under optimum reaction conditions. The increasing interest on halide perovskite photocatalysts over time as seen in Figure 1 caused accumulation of data in literature, which can be analyzed by machine learning tools to identify the path that leads to improved photocatalytic performance.

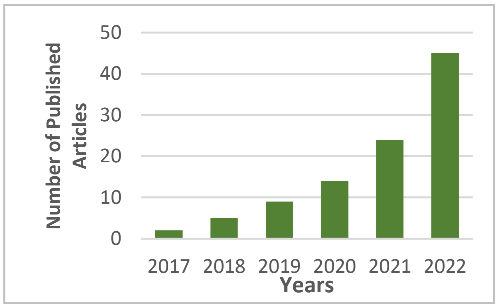

Figure 1. The Number of Published Articles on Photocatalytic CO_2 Reduction over Halide Perovskites

For this purpose, 115 articles published from 2017 to 2023 on photocatalytic CO_2 reduction over halide perovskites were studied to build a comprehensive database. The database consists of parameters such as perovskite type, crystal structure, particle size, band gap, catalyst preparation method, co-catalyst type and weight percent, light type, reaction phase, reaction medium and time. In addition, CO production rate was selected as output variable.

First, a simple descriptive statistics was used to identify the significant factors and major patterns in dataset to see their effects on production rate. Photocatalytic CO2 reduction reactions conducted in both liquid and gas phases. The analysis shows that performance of photocatalytic CO_2 reduction in liquid phase is better than that of in gas phase as it is evident from Figure 2. CO is the main product for both phases. Also, regardless of the reaction phase, halide perovskite photocatalysts favor gaseous products CO, CH_4, and H_2. In addition, the parameters such as perovskite composition, co-catalyst type, co-catalyst loading, and preparation methods directly are found to be effective in band gap, crystal structure, and hence performance of photocatalysts. Then, predictive models for CO production rate in both phases were developed using machine learning tools. The most influential variables for CO production were selected as descriptors for the models.

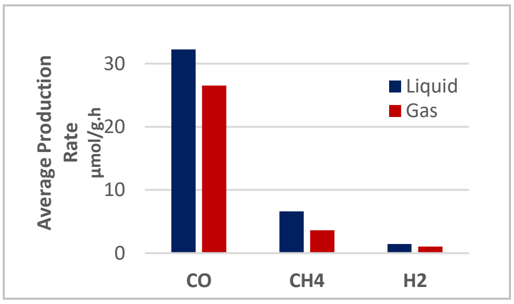

Figure 2. Average Production Rates for Products in Photocatalytic CO_2 Reduction over Halide Perovskites for Liquid and Gas Phase Processes.

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Machine learning analysis of photocatalytic CO_2 reduction on perovskite materials

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In recent years, the CO_2 emission to atmosphere has been increased with the increasing of the fossil fuel consumption and industrial developments. For a sustainable world, precautions such as reducing fossil fuels consumption, use of renewable energy resources and converting CO_2 to other more valuable chemicals should be considered (Kumar et al., 2020).

In this study, the aim was to analyze the photocatalytic CO_2 reduction on perovskites using machine learning on the dataset constructing from the literature until March 2023. The dataset consisted of 309 data from 62 articles; the samples were examined in the light of 29 variables (descriptors) and the total production yield (μmol.g^{-1}.h^{-1}) was used as the target variable.

The bandgap was predicted via linear regression and the yield analysis was done via decision tree, random forest, gradient descent, and association rule mining.

Linear regression was used to predict the missing bandgap values on python. The rest of the machine learning applications were done in R language. The decision tree was used to classify the total yield by *rpart* and *rattle* algorithms. The random forest was used to predict total yield by regression and *randomForest* used as the library. The gradient boosting library, *xgboost*, was also used to predict the total yield by regression. The association rule mining was done by the library, *arules* and the relation between the features and the output was obtained.

The dataset was divided into 2 parts according to the reaction phase (gas and liquid) and analysis was done separately.

For the bandgap prediction by linear regression, R-square are 0.97 and 0.75 for train and validation sets respectively as in Figure 1. The fitness of the model was quite good.

Association rule mining analysis shows that some properties of the experiments such as sonication as the synthesis method, short calcination time, Ru as the cocatalyst or Ba as a doped material have high probability to have high yield.

In the decision tree for the total yield classification, the cp and the minsplit was chosen as 0.015 and 5 for gas and liquid phase datasets. For gas data, the accuracy for train and test set are 0.89 and 0.76 respectively while these values are 0.87 and 0.84 for liquid data. The conditions leading to low total yield were are also predictable for both phase. The feature importance analysis shows that perovskite synthesis method and the type of perovskite are the most important features for gas and liquid phase respectively.

For random forest, R-square values are 0.77 and 0.64 for train and test set in gas phase respectively while these values are 0.77 and 0.49 in liquid phase. Band gap is the most effective feature for gas phase predictions while this was the cocatalyst in liquid phase.

Gradient boosting shows higher performance. For gas phase, the R^2 for training and testing were 0.95 and 0.65 respectively while they were 0.94 and 0.79and for liquid phase.

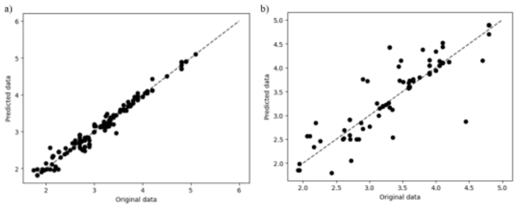

Figure 1. The original data versus predicted data for a) train set b) validation set

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Development of Z-scheme Heterojunctions for Photocatalytic Hydrogen Production

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Photocatalytic water splitting using solar light and water is one of the most promising methods for sustainable and renewable hydrogen production. In photocatalytic water splitting, water is principally decomposed into oxygen and hydrogen by a semiconductor, activated by solar light, forming electron-electron hole pairs. The photocatalytic water splitting mainly involves three steps, Fig. 1. These are [1] ;

i) Photoexcitation of semiconductor and generation of electrons and holes,
ii) Bulk diffusion and surface transfer of charge pairs
iii) iii) Consumption of the charge carriers in reduction and oxidation sites

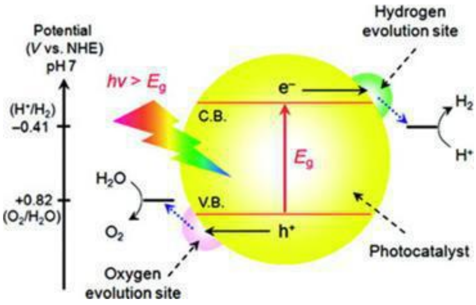

Fig. 1. The mechanism of photocatalytic water splitting [2].

The band gap of a semiconductor should cover -0.41 eV and 0.82 eV in order to participate in reduction and oxidation reactions to split water, Fig. 1 [2, 3]. Moreover, the band gap of the semiconductor needs to be between 1.3 eV and 3.1 eV in order to be excited by visible light, which belongs to the greater portion of solar light. However, the use of a single semiconductor typically cannot yield efficient hydrogen production due to problems such as electron-electron hole recombination, chemical instability in the aqueous medium, and low quantum efficiency of the semiconductor. Therefore, there is a number of studies concentrating on the modification of the band gap and the use of multiple photocatalysts to impede electron-electron hole recombination.

In the current study, Z-scheme heterojunctions based on g-$C_3N_4/TiO_2/CdS$ were systematically investigated to reveal their photocatalytic activity for hydrogen production. The photocatalysts synthesized were initially characterized by XRD, UV-Vis photo spectrometry, SEM, and BET to identify their crystal structures, band gaps, morphologies, and surface areas. The photocatalysts synthesized with different fractions were then subjected to photocatalytic tests under both UV (250-385 nm) and visible light (385-740 nm).

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Quantum efficiency of photocatalytic sea water splitting by Ag-AgI nanostructures

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Photocatalysis is a promising way to use and convert solar energy. As a result of multistage process under the action of radiation on the surface of the of the photocatalyst gaseous hydrogen and oxygen are synthesized which can be used in other field of industries and as fuel. Water is only one and sufficient reagent for obtaining green hydrogen. Electrolyte is one of the main elements of photocatalytic water splitting. It is the medium into which photogenerated electrons enter to reduce hydrogen, so the number of charges carries affects the water splitting efficiency. Sea water covers about 70% of the earth’s surface area. The use of sea water as a reagent for the use photocatalytic production of hydrogen fuel does not require the preparation of special electrolytes. In 1969 R. Horne determined the composition of sea water and proved the constancy of the composition almost anywhere in the world’s oceans. [1].

This nanoporous silver films has been synthesized by substitution reaction on a copper subtract from solution from silver nitrate (37.5 g/l $AgNO_3$). [2]. Partial iodide of the films in iodide vapor at room temperature was carried out to obtain Ag-AgI nanostructured composite, which is used as a photocatalyst. When an external voltage of 0.5-4 V was applied the appearance of photocurrent under the action of UV and visible radiation. 0.1M $NaNO_3$ was used as a model electrolyte and electrolyte with a composition close to the sea water composition as the investigated one. Sea water like electrolyte contains NaCl (7.58 w.%), $MgCl_2$ (1.06 w.%), $MgSO_4$ (0.46 w.%).

Quantum efficiency η is calculated as the ratio of the product of measument photocurrent I_{ph} and the photon energy to the product of the radiation power absorbed by sample surface P_{abs} and the electrone charge (1):

$$\eta = (I_{ph}\omega\hbar)(P_{abs}e)^{-1} \tag{1}$$

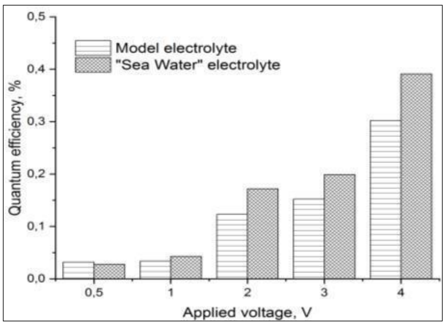

Figure 1. The dependence of quantum efficiency on applied voltage

Under the action of an applied voltage, the quantum efficiency of water splitting increases with increasing voltage. The electrolyte decomposition close to the composition of sea water contains more charge carries, so the electrical conductivity of this electrolyte is higher in compare with model electrolyte. At an applied voltage of 4V with a model electrolyte, the quantum efficiency was 0.3% and when using “sea water” electrolyte – is 0.4%. The average quantum efficiency of water splitting increase with the application voltages of 0.5-4 V was 23%.

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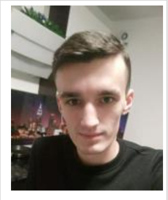

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Effect of A-site dopant on hydrogen La$_{1-x}$M$_x$Al$_{1-y}$Mn$_y$ (M=Na and Sr) perovskite oxides for thermochemical water splitting applications

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The study focuses effect of A-site substitution on the structural properties of La$_x$Na$_{1-x}$Al$_y$Mn$_{1-y}$-La$_x$Sr$_{1-x}$Al$_y$Mn$_{1-y}$ (x=0.2, 0.4, 0.6, 0.8, y=0.2, 0.4, 0.6, 0.8) (Na-Sr) perovskite oxides were synthesized by the Pechini method to observe the effect of structural properties on hydrogen production. Na was used as the A-site dopant, which was studied for the first time [1].

8 different compositions in the LNAMn, LSAMn oxide family evaluated by the water splitting test. Figure 1 shows that oxygen production capacities of given perovskite oxides.

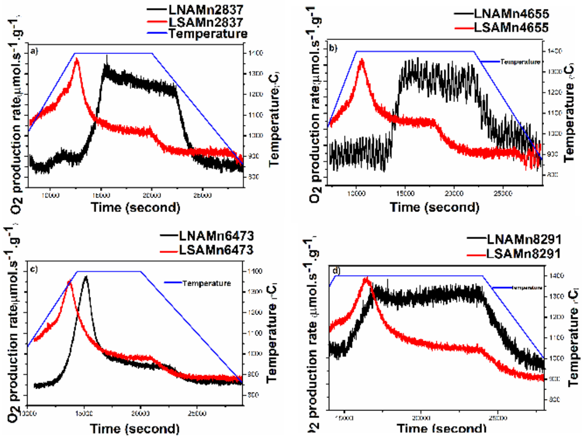

Figure 1. The O_2 production rate-time profiles a) LNAMn2837 and LSAMn2837 b) LNAMn4655 and LSAMn4655 c) LNAMn6473 and LSAMn6473 d) LNAMn8291 and LSAMn8291 perovskite oxides.

The areas under the curves are also the total O_2 gives the amount of formation. All the studies carried out O_2 formation were determined in the compositions, Table 1.

Table 1. O_2 production in LNAMn and LSAMn perovskite oxides.

Perovskite Oxide	First O_2 Temperature (°C)	O_2 Amount(µmol)
LNAMn2837	600	159
LNAMn4655	880	328
LNAMn6473	1100	340
LNAMn8291	900	374
LSAMn2837	1350	696
LSAMn4655	1330	642
LSAMn6473	1400	494
LSAMn8291	1400	641

According to these data, it was determined that more O_2 production was observed in the Sr-doped perovskites compared to Na-doped ones. than the Na ones. Similarly, the H_2 production capacities were determined at 800°C by the thermochemical water splitting test, Figure 2.

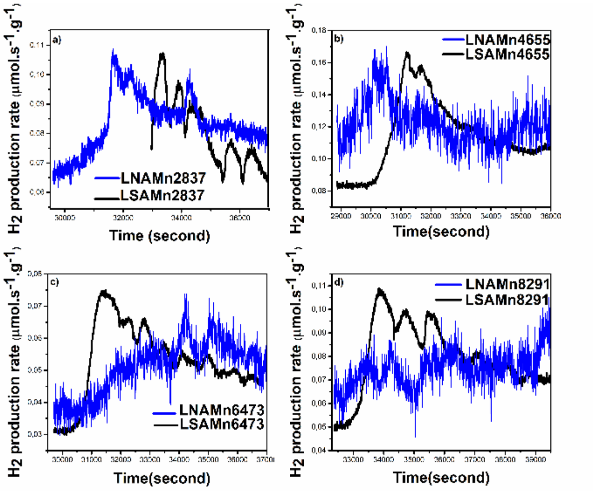

Figure 2. The H_2 production rate-time profiles a) LNAMn2837 and LSAMn2837 b) LNAMn4655 and LSAMn4655 c) LNAMn6473 and LSAMn6473 d) LNAMn8291 and LSAMn8291 perovskite oxides.

H_2 production was observed in all the compositions considered. All of the studies carried out H_2 formation was determined in the compositions, Table 2.

Table 2. Values obtained during H_2 formation from perovskite powders.

Perovskite Oxide	H_2 Amount(µmol)	H_2/O_2 (µmol/g)	H_2/O_2 (%)
LNAMn2837	54	0.33	67.92
LNAMn4655	30	0.09	18.29
LNAMn6473	26	0.07	15.29
LNAMn8291	29	0.07	15.51
LSAMn2837	84	0.12	24.14
LSAMn4655	254	0.39	79.13
LSAMn6473	164	0.33	66.40
LSAMn8291	218	0.34	68.02

Redox activities for the compositions were obtained as approximately 79%, 66%,68%, and 67% for LSAMn4655, LSAMn6473, LSAMn8291, and LNAMn2837, respectively. It has been observed that Sr^{2+} element, which is the A-site doping element, plays a dominant role on hydrogen production.

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Electrochemical fabrication and reductive Li-doping of TiO_2/ERGO nanocomposite as photoanode for photoelectrochemical water-splitting

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Production of H_2 as a sustainable and clean energy source by photocatalytic or photoelectrochemical water splitting is one of the most promising ways to solve the problems of energy and environmental pollution. TiO_2 has been one of the most researched materials as a photocatalyst in the photocatalytic water-splititng into H_2 and O_2. It is used in solar cells, batteries, supercapacitors, the removal of air and water pollution, and water-splitting into H_2 as a photocatalyst[1]. Also, TiO_2 combined with graphene derivatives has become a great research interest as potential photoanode material for diverse applications in photocatalysis and solar energy conversion due to providing high surface area and improving carrier mobility.

In this study, it was aimed to fabricate a photoanode that can operate in the entire spectrum of the sun for effective photoelectrochemical water-splitting by shifting with electrochemical reductive self-doping the wide band gap of TiO_2/ERGO nanocomposite which produced by co-electrodeposition technique which is a simple, one-pot, and environmentally friendly directly on FTO. TiO_2/ERGO nanocomposites were doped as electrochemically reductive in the presence of Li^+ cations to form Ti^{3+} defects and O vacancies in the structure[2]. Then these doped electrodes were characterized by XRD, XPS, and FESEM techniques in terms of composition, structure, and morphology. The improvement in photoelectrochemical efficiency of the doped TiO_2/ERGO structures in the visible region was determined by photocurrent density measurements, UV-vis-DRS, and EIS techniques. Then, Li-doped TiO_2/ERGO-FTO photoanodes with high activity under visible light will be used in the production of H_2 gas by photoelectrochemical water-splitting without any bias-voltage.

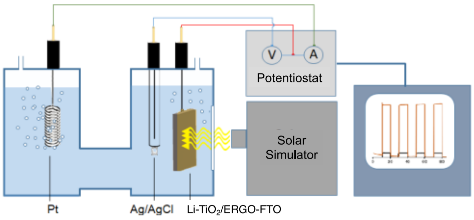

Figure 1. Determination of photoactivity of Li-TiO_2/ERGO-FTO photoelectrodes in water-splitting.

FESEM images of the Li-TiO_2/ERGO electrode prepared by reduction from the $LiClO_4$ solution are given in Fig. 2a. It was observed that the nanocomposite structure consisting of TiO_2 and graphene did not deteriorate and was preserved exactly after Li-doping.

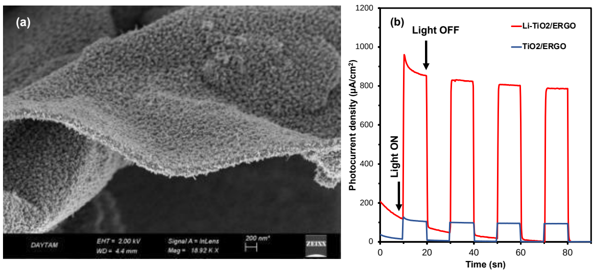

Figure 2. FESEM images of Li-TiO_2/ERGO (a) and photocurrent responses in 0.5 M KOH of TiO_2/ERGO and Li-TiO_2/ERGO photoelectrodes (b)

Photocurrent response of photocatalysts as shown in Fig. 2b, in a 3-electrode cell where the Pt electrode is used as the counter, Ag/AgCl electrode as the reference and the Li-TiO_2/ERGO-FTO nanocomposite electrode as the photoanode, in 0.5 M KOH aqueous solution, the photoanode in the solar simulator (AM1.5G, $100 mWcm^{-2}$) and the resulting photocurrent was measured with a potentiostat depending on time (I-t). Almost 10-fold increase in photocurrent densities was observed after electrochemical reductive doping.

It is expected that Li-TiO_2/ERGO-FTO nanocomposites will reach 25 $\mu mol.h^{-1}cm^{-2}$ solar-hydrogen conversion (STH) efficiency in the visible region for water-splitting as photoanode.

Acknowledgements

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Enhanced visible light photoactivity of Magnesium-doped TiO_2/ERGO nanocomposite electrodes for efficient photoelectrochemical water splitting

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Titanium dioxide (TiO_2) is a stable semiconductor photocatalyst that absorbs photons when exposed to ultraviolet (UV) light and produces electrons (e^-) and holes (h^+) that can participate in chemical reactions. TiO_2 is a vital semiconductor material in photoelectrochemical (PEC) water splitting, enabling the conversion of sunlight into clean and renewable hydrogen fuel. However, due to its high band gap energy of TiO_2 (3.2 eV), reducing the band gap energy by doping TiO_2 with narrow band gap materials has attracted great research interest in recent years. When TiO_2 interacts with light to form an e^- and a h^+, they quickly recombine instead of producing a chemical reaction or electric current, producing a photon or heat, limiting the efficiency of photocatalysts. To overcome this limitation, TiO_2 is doped with different metals and nonmetals [1]. This doping provides additional energy states in the band gap of TiO_2 that can trap electrons or holes and prevent recombination.

In this study, TiO_2 and reduced graphene oxide (ERGO) nanocomposite electrodes on fluorine doped tin oxide (FTO) transparent conductive glass were synthesized in one step by an economical and environmentally friendly electrochemical method that we improved earlier [2]. Then, these electrodes were converted into TiO_2/ERGO nanocomposite structures doped with Mg with Ti^{3+} defects and O cavities in the structure by electrochemical reduction in an electrolyte containing alkaline earth (Mg^{2+}) metal cations without using high temperature, toxic reducing agents or high pressure hydrogen. It is thought that doped Mg^{2+} ions narrow the wide band gap of TiO_2 and increase its photoactivity in the visible region, as well as improve charge transfer at the interface and decrease the recombination rate. Characterization of the obtained samples in terms of composition, structure and morphology was performed using X-ray Diffraction Spectroscopy (XRD), Scanning Electron Microscopy (SEM) (Figure 1), X-ray Photoelectron Spectroscopy (XPS) and Energy Dispersion Spectroscopy (EDS). Electrochemical analyzes were performed with cyclic voltammetry (CV), linear sweep voltammetry (LSV) and chronoamperometry. The activity and photoelectrochemical efficiency increases in the visible region of doped TiO_2/ERGO structures were determined by photocurrent density, and UV-VIS. Doped TiO_2/ERGO-FTO electrodes, which have high activity in the visible region, will be used for photoelectrochemical water splitting without applied any bias voltage (Figure 2).

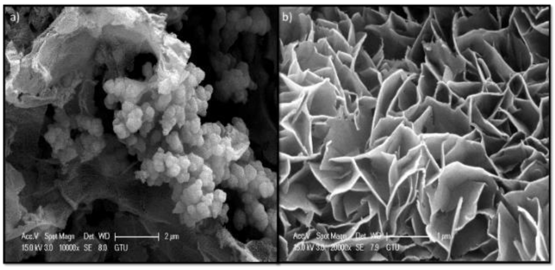

Figure 1. SEM images of TiO_2/ERGO (a) and Mg-TiO_2/ERGO (b) electrodes

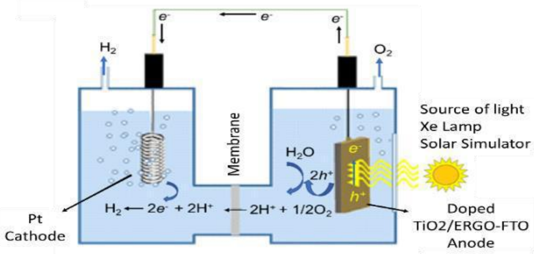

Figure 2. Mechanism for H_2 production from external potential application of TiO_2/ERGO-FTO electrodes

Acknowledgments

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Electrocatalytic Properties of Sb_2Se_3 Thin Films in Water Electrolysis

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Water electrolysis is the most attractive method for obtaining environmentally friendly hydrogen. As you know, during the electrolysis of water, water molecules are separated into hydrogen and oxygen molecules using a current flowing through water. This process requires quite a lot of energy, so the use of electrocatalysts can significantly increase the efficiency of this process.

Research is often carried out in the field of electrocatalysis of metal chalcogenides as a cathode in the electrolysis of water [1]. In particular, antimony selenide (Sb_2Se_3) [2] is a semiconductor material that has been studied as a potential electrocatalyst for hydrogen evolution during water electrolysis. The electrocatalytic properties of Sb_2Se_3 thin films during water electrolysis have been studied in several studies [3, 4]. These studies have shown that Sb_2Se_3 exhibits good catalytic activity in the hydrogen evolution reaction (HER). The researchers attributed this activity to the high conductivity and good stability of the Sb_2Se_3 film.

In general, the electrocatalytic properties of Sb_2Se_3 thin films in the electrolysis of water open up prospects for the development of efficient and stable cathodes in the process of water and hydrogen ion reduction. However, more research is needed to optimize the synthesis and performance of this material.

For the study of the electrocatalytic characteristics, thin Sb_2Se_3 semiconductor films were obtained by electrochemical deposition from an aqueous and organic electrolyte with a tartrate additive [5–9]. The samples were obtained on a nickel substrate with an area of 2 cm^2.

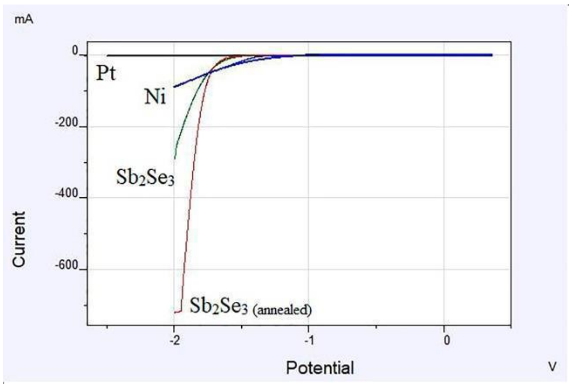

Figure 1. Study of the electrocatalytic activity of synthesized Sb_2Se_3 thin films in a neutral medium (0.5 M Na_2SO_4).

The electrocatalytic activity of the synthesized thin Sb_2Se_3 films was studied in a neutral medium (0.5 M Na_2SO_4). In this case, the surface area of the platinum electrode was 0.35 cm^2, and the surface area of the nickel electrode and the samples obtained on it was 2 cm^2.

As can be seen from the figure, compared with other cathodes, annealed Sb_2Se_3 has high electrocatalytic activity. Annealing of samples on a nickel electrode was carried out at a temperature of 723 K, in an atmosphere of inert gas - argon 70 minutes. The increase in electrocatalytic activity is due to changes in the structure of the studied material during heat treatment. This can lead to an increase in the number of active sites, or reduce the impurities' content and improve the material's crystal structure.

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Hydrogen evolution reaction from brass nanostructures

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With the increasing population and rise of energy-consuming lifestyles, the novel ways of energy production technologies trigger more and more attraction. Among them, the production of hydrogen plays a crucial role especially the production of green hydrogen. Metal oxide nanocomposites are widely used in various fields of science and technology, such as gas sensors, photocatalysts, electrocatalysts and electrochemical sensors. Oxide materials derived from copper and zinc found their application in numerous catalytic processes thanks to their accessibility, reasonable price and adaptability. It has been reported that the ZnO-CuO or CuO-ZnO nanocomposite systems are studied for water splliting and hydrogen evolution properties, as well as their photocatalytic activity and electrochemical sensing [1,2]. In comparison to other synthesis methods, electrochemical CuZn oxidation quickly forms nanostructured oxide film on the electrode surface and allows good control of morphological properties.

In this study, electropolished brass was anodized in 1.0 M NaOH with the addition of 10^{-4} M potassium permanganate $KMnO_4$ as an oxidation booster. Anodization was performed using potentiostat and a three-electrode system in order to form nanostructures. The morphology of CuZn alloy surface depends on the applied potential [3].

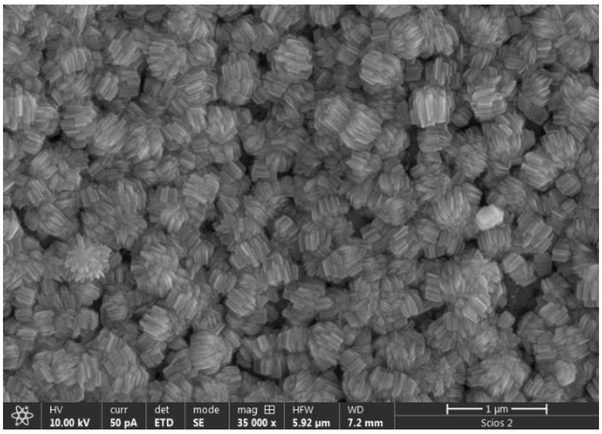

Figure 1. Morphology obtained during potentiostatic oxidation of CuZn alloy in 1M NaOH and 10^{-4}M $KMnO_4$ at 100mV

SEM micrograph shows barrel-like structures which are formed when 100mV potential is applied. It has been shown that the morphological properties of the samples are the predominant factor that has to be controlled to develop a good catalyst for hydrogen evolution reaction.

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XPS studies of copper oxides as catalysts for hydrogen generation

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Hydrogen has appeared as an alternative fuel to replace fossil-fuel-based energy sources. Hydrogen is abundant but finding it in a free state is impossible. Due to its highly reactive nature, hydrogen does not exist freely. Green hydrogen can only be produced from electrolysis and other electrochemical reactions. Conversion of electricity or solar energy into chemical fuels via water splitting is a great challenge and the design of highly efficient and low-cost catalysts for hydrogen evolution reaction (HER) has attracted great attention [1]. In the current research, electropolished copper was anodized in 1.0 M NaOH, using a potentiostat and a 3-electrode system in order to form nanoneedles. The major novelty in the research was the application of electrolyte additives, enhancing the formation of the nanostructured passive oxide layer. Potassium permanganate, $KMnO_4$ was used as an oxidation booster during anodizing. Application of even 10^{-4} M $KMnO_4$ in 1.0 M NaOH was found to be advantageous for the nanostructured formation. The obtained materials were found to be promising for photoelectrochemical water splitting. Preliminary research reveals that thanks to the composition and morphology of the oxide efficient H_2 generation is possible. Figures 1 and 2 show detailed XPS spectra of Cu2p 3/2 and O1s, respectively. As can be seen from Fig. 1, Cu2p 3/2 spectrum on the lower binding energy side can be described by one peak which according to peak shape, binding energy position of 934.6 eV and position of modified Auger parameter (not shown here), can be subscribed to Cu(II) signal of $Cu(OH)_2$ which is furthermore supported by the presence of several shake-up signals above 938 eV on the left-hand side of the spectrum, which are only characteristic of the copper in 2+ oxidation state. This finding is additionally supported be O1s spectrum in Fig. 2 which generally can be described by one peak from the hydroxyl group.

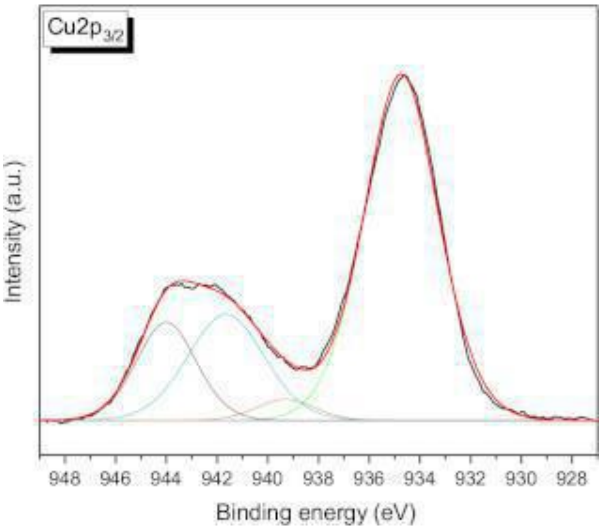

Figure 1. XPS spectrum of Cu 2p 3/2 in CuO

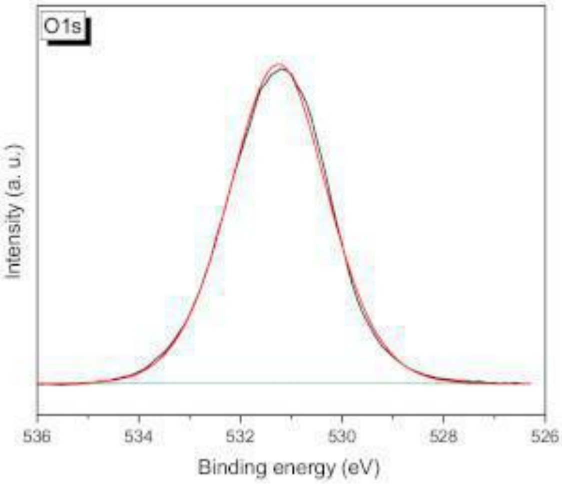

Figure 2. XPS spectrum of O1s in CuO

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Development of High Entropy Perovskite Oxides for Thermochemical Water Splitting

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Environmental pollution caused by fossil fuels is becoming more and more important to us day by day. Therefore, renewable energy sources and environmentally friendly energy production methods are gaining more and more importance day by day in order to reduce the problems that arise as a result of climate change(Sharma et al., 2021). One of the prominent energy sources in this regard is Hydrogen energy. Since hydrogen gas is a clean energy source that does not contain carbon, it is considered one of the most suitable sources for renewable energy.

Hydrogen is a promising energy source because it is abundant in nature. Hydrogen can be obtained in many ways. One of these methods is the Thermochemical water separation method(Osman et al., 2022). This method uses concentrated solar energy to carry out pure redox reactions, and hydrogen can be produced without the need for any purification, that is, it does not require catalysis to perform chemical reactions.(PİŞKİN, 2021)Perovskite oxides come to the fore due to their superior structural stability. It provides many advantages with its unique compositions, microstructures and adjustable properties. They are active substances that can be used in TWS reactions, thus positively affecting the hydrogen production efficiency.

In this context, $La_{0.7}Sr_{0.3}Cr_{0.2}Mn_{0.2}Fe_{0.2}Ni_{0.2}X_{0.2}O_3$ (LSCMFNX) (X=V,Ti,Co)based perovskite oxides were studied in this study. LSCMFNX powder was synthesized by Sol-gel-based Pechini method. As starting chemicals, nitrates of all of the considered cations were used: La(NO3)3·6H2O, Sr(NO3)2, Co(NO3)2·6H2O, Fe(NO3)3·9H2O, Mn(NO3)2·4H2O and Ni(NO3)2·6H2O, NH4VO3, $Co(NO_3)_2·6H_2O$, $Ti(NO_3)_4$. Primarily, the stoichiometric amount of the metal nitrate precursors were dissolved in distilled water, then citric acid and ethylene glycol were added into the solution. The molar ratio of all the cations, citric acid, and ethylene glycol in the mixture was 1:2:4. The solution was heated up to 70°C with continuous stirring by the help of the magnetic stirrer to drive the esterification reactions. The resulting gel was dried at 250°C for 2 hours to remove residual organics and nitrates. The dried gel was calcined at 700°C, 850°C,1000°C, 1150°C and 1300°C for 6 hour. The resulted structures were characterized with respect to their crystal structure and particle size and candidate materials are selected for using TWS redox reactions

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Investigation of capacitive and photocatalytic properties of FTO-ERGO/TiO_2/Al nanocomposites for energy applications

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Photocatalysts have been studied in many application areas in recent years due to their high activities, stabilities, and low toxicities. Especially, the discovery of the use of titanium dioxide (TiO_2), a semiconductor, as a photocatalyst in water splitting has attracted great interest for the effective utilization of solar energy. Titanium dioxide, due to its suitable band edge positions, high chemical stability, high optical absorption, and photocorrosion resistance, as well as its low cost, is widely used in photocatalytic material studies. However, TiO_2 has disadvantages such as rapid recombination of photo-generated charge carriers and its ability to be active in only a small part of the solar spectrum, the UV region, due to its wide bandgap. Therefore, improvements can be made by doping metal oxides like TiO_2 with metals or non-metals. It is believed that the doping ions narrow the wide bandgap of TiO_2, increasing its photoactivity in the visible region, while also improving charge transfer at the interface and reducing recombination rates. Literature shows that TiO_2 composite structures doped with graphene and reduced graphene oxide exhibit higher photoactivity compared to graphene-free structures. Additionally, it is known that doping TiO_2 with metals such as lithium, sodium, potassium, magnesium, and aluminum increases the electron transfer rate and enhances the photocatalytic effect.

TiO_2 is also widely used in supercapacitor applications. Supercapacitors are widely used in portable electronics and electrochemical energy storage as they have higher energy density, fast charge-discharge capacities, long cycle stability and higher power density than electrostatic capacitors and batteries. But, TiO_2 has high band gap energy and low electrical conductivity that limit its performance. To overcome these limitations, researchers have focused on incorporating carbon-based materials, particularly graphene, into TiO_2 nanocomposite structures. Graphene is highly abundant and possesses excellent electrical conductivity and chemical stability. It has been observed that the electrical conductivity of TiO_2 can be improved by introducing metals capable of creating donor or acceptor states within the band gap, thereby increasing the concentration of charge carriers [1]. In this study, the addition of aluminum under optimized conditions to the FTO-ERGO/TiO_2 nanocomposite structure is expected to result in a well-structured surface with enhanced charge storage capabilities.

In this study, FTO-ERGO/TiO_2 nanocomposite structures are obtained by the electrochemical reduction of graphene, which is an environmentally friendly method that does not involve toxic chemicals [2], and followed by electrochemical doping of the surface with aluminum, as seen in figure 1. TiO_2 decorated with electrochemically reduced graphene oxide forms three-dimensional, well-structured surfaces that enhance the scattering and interaction of photons on the surface. This increases the conductivity of the surface and reduces the probability of recombination.

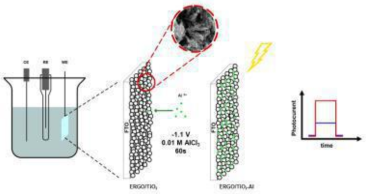

Figure 1. The schematic representation of production of FTO-ERGO/TiO_2/Al nanocomposite electrodes.

The nanocomposites were characterized in terms of their composition, morphology, and structure using Scanning Electron Microscopy (SEM), X-ray Diffraction Spectroscopy (XRD), and X-ray Photoelectron Spectroscopy (XPS). To assess their electrochemical properties, cyclic voltammetry (CV), linear sweep voltammetry (LSV), and chronoamperometry techniques were employed for electrochemical analysis. Photoelectrochemical responses under illumination were obtained without the application of an external potential, and as a result, doping parameters were determined under optimum conditions. According to the photoelectrochemical responses, the FTO-ERGO/TiO_2/Al nanocomposite structure, which exhibited the highest photoactivity, generated a current of 316 $\mu A/cm^2$ compared to the undoped structure. The optimized nanocomposite structure was utilized in the photocatalytic degradation of methylene blue. A decrease in the absorption peak intensity at the characteristic wavelength of 665 nm, which corresponds to the characteristic absorbance of the dye, was confirmed by UV Spectrometry during the photocatalytic degradation.

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HYDROGEN STORAGE & SEPARATION

Reversibility of solid-gas and electochemical hydrogenation of Ti-based AB-type alloys studied by in-situ neutron diffraction

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Most metals can react with hydrogen to form either very stable or unstable metal hydrides. First ones, classed as *A*-type, comprise alkali, alkali-earth, rare earth and early transition metals. Their hydrides need to be heated well above room temperature to desorb hydrogen near atmospheric pressure. Second ones, classed as *B*-type, are late transition metals and *p*-type elements. Their hydrides are only formed at hyperbaric pressures well-above 100 atm. The association of *A* and *B*-type metals to form AB_n intermetallics allows reversible hydrogen storage at normal conditions of pressure and temperature [1].

Ti-based *AB* intermetallics are remarkable materials for hydrogen storage as they are so far the best compromise between capacity and reversible loading at room temperature while keeping affordable cost. The association between *A*-type titanium metal and *B*-type late transition 3*d* metals such as Fe, Co and Ni offers not only the possibility to store large amounts of hydrogen but also to tune, through chemical substitutions, their thermodynamic properties [2]. Disregarding the remarkable exception of TiNi that exhibits polymorphism and shape memory properties, all Ti-based *AB* intermetallics crystallize in the cubic CsCl-type structure [3].

In this presentation, hydrogenation properties of Ti*B*-type intermetallics (*B* = Fe, Co and Ni) will be reviewed with focus on the Ti(Fe,Mn) and Ti(Ni,Cu) systems and their application for large-scale solid-gas hydrogen storage [4] and as negative electrodes of Ni-*M*H batteries [5], respectively. The use of in-situ neutron diffraction to unveil hydrogenation mechanisms [6], as shown in Figure 1 for the Ti(Fe,Mn) system [7], will be particularly highlighted.

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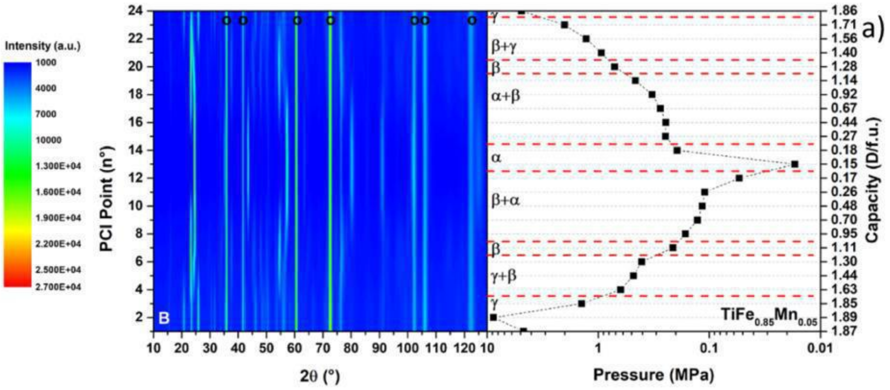

Figure 1: In situ neutron diffraction 2D patterns (counter plot, λ = 1.286 Å) and PCI curve at RT during deuterium desorption /absorption between 0.02 and 9 MPa for $TiFe_{0.85}Mn_{0.05}$ alloy.

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Metal hydride — carbon composites: advanced materials for hydrogen energy technologies

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The main priority in advancing environmentally friendly energy technologies is development of efficient materials for energy storage and conversion including metal hydrides (MH). Advantages of MHs include very high energy storage density per unit volume, tunable composition-dependent thermodynamics of the reversible interaction of the parent hydride-forming material with hydrogen, both from the gas phase and electrolyte, technological flexibility in various niche applications, and many other useful features.

At the same time, successful implementation of MH based energy technologies requires solution of a number of challenging problems including improvement of hydrogenation/dehydrogenation kinetics, prolongation of the cycle lifetime, increase of effective thermal (electric) conductivity to improve performances of the upscaled gas phase (electrochemical) systems, mitigation of stresses which appear in the MH bed due to increase of its volume upon hydrogenation, etc.

Many of these problems can be solved by the creation of composite or hybrid materials containing MH filler and additives which combine several useful features (catalysis of H transfer reactions, high electric and thermal conductivity, plasticity, possibility to envelop MH particles thus preventing their oxidation and sintering) with minimal decrease of hydrogen storage capacity.

MH-based composites, powder mixtures or compacts containing various forms of carbon additives prepared from solid or gaseous feedstock and taken in minor (1–3 wt.%) amounts, allow to achieve maximum benefits in gas phase and electrochemical applications (Figure 1).

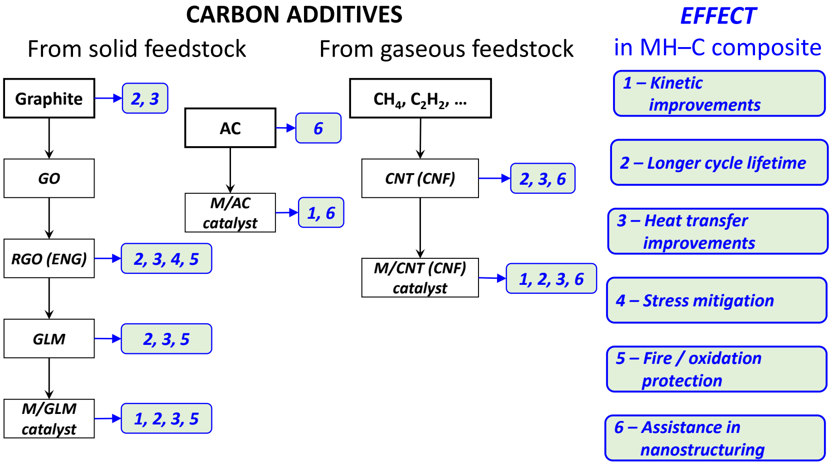

Figure 1. The most frequently used carbon additives in metal hydride – carbon composites and their beneficial effects.

This presentation summarizes results of R&D activities of the research teams from FRC PCP&MC RAS in Russia and HySA Systems in South Africa in the development of advanced MH based composites with carbon additives including activated carbon (AC), graphite, expanded natural graphite (ENG) or reduced graphite oxide (RGO) prepared from graphite oxide (GO), graphene-like materials (GLM), carbon nanotubes (CNT) and nanofibres (CNF), as well as efficient hydrogenation/dehydrogenation catalysts prepared by the deposition of metal nanoparticles (M=Ni, Pd) onto the carbon supports. The developed materials have been integrated in various hydrogen energy storage applications including advanced MH containers for hydrogen storage and compression and MH electrodes for NiMH batteries.

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Utilization of waste aluminum for hydrogen production and material recycling

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Waste management and energy production are crucial fields for ensuring global sustainability. The increasing demand for aluminium in Europe, estimated to rise by 40 percent by 2050, underscores the need for effective waste management and the transition towards a circular economy [1]. Although recycling efforts have been made, a considerable quantity of aluminium waste still ends up in landfills, causing environmental pollution. Therefore, there is a pressing need to develop novel approaches to reduce the landfilling and waste of aluminium. This study aims to explore innovative scientific and engineering activities to harness the potential of waste aluminium for electricity generation through hydrogen production using the reaction between waste aluminium and water. The by-product obtained from this reaction can be further recycled back to aluminium through carbon-free electrolysis or utilized as a precursor to produce valuable materials.

This study proposes a novel concept (Figure 1): the utilization of low-value aluminium waste, such as powder, scraps, foil, wire, and product packages, for on-demand hydrogen production through reactions with water. These reactions yield 0.11 kg of hydrogen and approximately 4.3 kWh of heat per kilogram of aluminum [2]. The by-product of the reaction, mainly aluminium hydroxide ($Al(OH)_3$), can be recycled through an innovative carbon-free electrolysis process or serve as a precursor for the production of ceramics, enhancing overall efficiency and economic viability. This closed-loop approach offers the opportunity to generate electricity, heat, and valuable materials from otherwise underutilized waste aluminium. Hydrogen, as an energy carrier, offers an opportunity to replace fossil fuels and reduce atmospheric pollution. The proposed hydrogen production method using waste aluminium addresses the challenges associated with hydrogen storage by enabling real-time, on-demand hydrogen production and utilization.

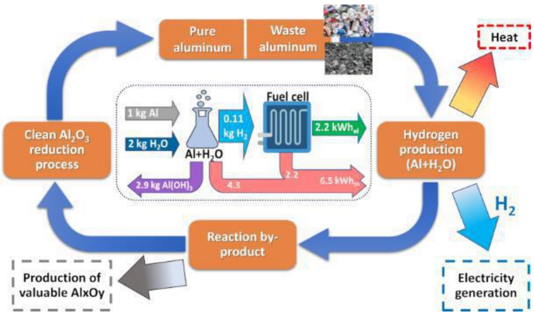

Figure 1. Recycling of waste aluminum and energy generation.

The formation of a thin protective oxide layer on aluminium's surface inhibits its reaction with water. Various strategies, such as the addition of hydroxide promoters (e.g., NaOH or KOH), aluminium oxide (Al_2O_3), salt promoters (e.g., NaCl or KCl), or activation by alloying, can disrupt the oxide layer and enable the aluminium-water reaction [3]. Notably, NaOH has been commonly used as the efficient promoter.

Several factors can influence the kinetics of the aluminium-water reaction: temperature, alkali concentration, water amount, aluminium mass, the ratio of aluminium to alkali concentration, and the heat dissipated during the reaction. The study's results indicate that temperature, in particular, plays a significant role in the reaction kinetics. Proper thermal insulation of the reaction vessel can even enhance the hydrogen production process by utilizing the heat generated in the exothermic reaction. Insulating the reaction vessel leads to self-promoted hydrogen production as the exothermic reaction produces heat inside the vessel. The activation energy for NaOH solution was calculated as 48.1 kJ/mol using the Arrhenius equation. Furthermore, the study investigates the reaction mechanism and analyzes the structure of the reaction's by-product at different stages. The analysis revealed that the by-product obtained from the alkali solution and dried under ambient conditions contains a substantial amount of thermonatrite, which results in a relatively low surface area (1-2 m^2/g). Therefore, to prevent contamination and enhance the surface area to over 200 m^2/g, an additional step of rinsing the by-product with distilled water is necessary.

Acknowledgements

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Hydrogen processing as a way of producing fine metallic powders

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Hydrogen (H) commonly undergoes reactions with metallic elements forming metal hydrides (M-H) since metals can exhibit hydrogen diffusivity comparable to that of ions in aqueous solutions, allowing thermodynamic equilibrium to be attained relatively quickly, even at room temperature [1]. The capacity of hydrogen to form metal-hydride systems is generally attributed to its (a) moderate electronegativity, (b) small atomic size, and (c) low nuclear mass [2]. Metal lattices accommodate H atoms typically at their interstitial sites by going through fundamental changes in the crystal structure leading to the formation of different phases metal-hydrogen systems [2]. H atoms can be densely packed in metal hosts through a large exothermic reaction such that the density of hydrogen can surpass that of liquid hydrogen. The aforementioned factors stimulate the utilization of metal hydrides for energy storage purposes [3].

The impact of H on metals can be examined from various perspectives. Hydrogen embrittlement (HE) is a detrimental phenomenon for structural metals, as it can proceed to sudden failure even at low stress levels and concentrations of H. Conversely, the embrittlement is regarded as a convenient method for producing finely divided metal powders of transition and rare-earth (RE) metals which exhibit brittleness after H absorption. The brittle nature of H absorbing metallic systems stems from the significant volumetric changes that occurs during the formation of solid solutions and/or hydrides. Intermetallics such as $LaNi_5$, $SmFe_3$ and TiFe display high H absorption capacity and exceptional lattice expansion around 27.4%, 19%, and 18.8% respectively which results in the decrepitation of the material into fine powder form readily [4]. Hydrogen decrepitation (HD) is also a widely used route to obtain sinterable powders for strong permanent magnet production (e.g., $Sm_2(Co,Fe)_{17}$, $Nd_2Fe_{14}B$). Nd-Fe-B alloys become H hardened due to the formation of a Nd-rich hydride phase and disintegrate upon milling methods [5].

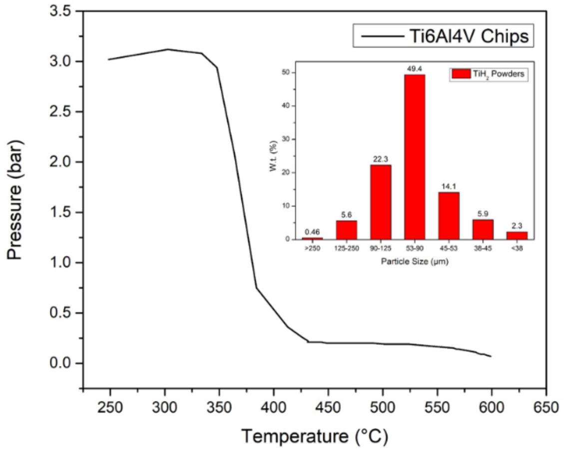

Figure 1. Hydrogenation process of Ti6Al4V chips

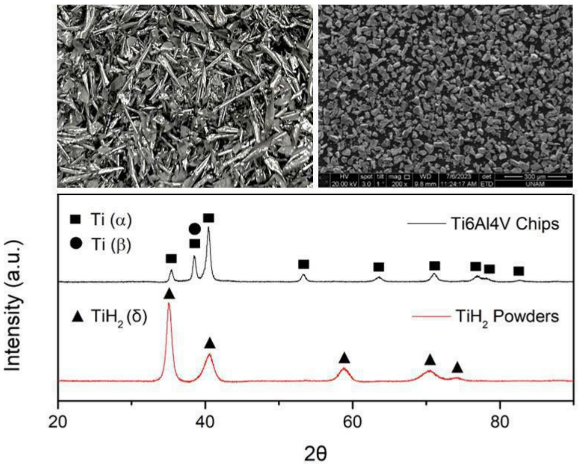

Figure 2. XRD spectra of hydrogenated Ti6Al4V powders

The elemental metals such as Pd, Ti, Zr also accomodate large amount of H in their lattice sites without losing their integrity. Therefore, most M-H systems require further mechanical force to form powders similarly to magnetic compounds.

In this study, Ti-H system is investigated by using a titanium alloy. Ti6Al4V chips are cleaned and hydrogenated at 650°C for 1.5 hours in a stainless-steel vessel. Then, the vessel is air cooled overnight for the formation of brittle TiH_2 phase. After, the chips are ball-milled for 30 minutes for the fragmentation process. Last, the powders are sieved and characterized. According to Figure 1, the hydrogenation started around 340°C and continued until the chips are fully hydrogenated. 50% of the powders were in between 53-90 μm and there were also particles below 38 μm. XRD spectra of the powders shows that there is only TiH_2 phase present without any α or β phases (Fig.2.).

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Experimental studies and DFT modeling of hydrogen sorption behaviour of Mg-based nanostructured composites and nanosized clusters

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Magnesium as a material for reversible hydrogen storage attracts a lot of attention from researchers over many decades due to the high mass content of hydrogen in the hydride MgH_2 (7.6%). Yet, its wide practical application is hindered by several drawbacks, the main of which is the slow kinetics of hydrogen sorption and desorption (s/d).

An effective way to solve this problem is to create Mg-based materials, in which the improvement of hydrogen s/d kinetics is achieved by introducing catalytic additives (3*d* metals) and simultaneous reduction of the grains of the magnesium phase to submicro- and nanosizes (nanoconfinment) [1]. Since experimental studies of subnano- and nanosized magnesium particles often face practical difficulties, quantum chemical (mostly DFT) calculations can provide valuable information for a purposeful development of advanced Mg-based hydrogen storage nanomaterials [2].

This report summarizes results of recent R&D activities [1–5] of the research teams from FRC PCP&MC RAS on the creation of novel Mg-based materials with improved hydrogen s/d kinetics. These R&Ds are featured by original approach lying in the combination of experimental studies and quantum chemical calculations, the objects of which, respectively, are nanostructured Mg-based materials and subnanosized Mg clusters, as well as in the search for correlation between the results obtained on studying those objects that are quite different in size and morphology.

Mg-based materials with enhanced hydrogen s/d behavior are powder composites of Mg-Ni alloys with nanocarbon additives prepared by high-energy ball milling under hydrogen. The particle morphology and microstructure of thus prepared composites allows achieving the nanostructured state of Mg phases and increasing the area of interphase boundaries; Ni-containing phases effectively serve as catalysts of H_2 molecules scission and H atoms transfer; nanocarbon additives make it possible to stabilize the nanostructured state during the hydrogen s/d processes and improve heat transfer in the powder composites.

The DFT calculations of the potential energy surfaces elementary hydrogenation reactions of Mg_{18} and 3*d*-metals doped $Mg_{17}L$ (L = Ti, V, Cr, Mn, Fe, Co, Ni) clusters were performed within the BP86 approximation using the GAUSSIAN-09 program with the 6-31G* basis set. The geometric, vibrational, energy, and electronic characteristics of the intermediates and transition states along the minimum energy pathways of these reactions were determined, the activation barriers and energy changes at their key stages were evaluated, and the effect of the dopant nature on these characteristics as L varied along the 3*d*-period was analyzed.

Further comparison of the results of DFT modeling and qualitative conclusions for small Mg clusters with those for families of larger ones [4] suggests the validity of extending DFT approaches to even larger nanosized clusters with a higher content of dopant atoms. In this regard, the results of experimental studies correlate with the data obtained in DFT modeling, which show that the rate-limiting step of the $Mg_{17}L + H_2 \rightarrow Mg_{17}LH_2$ catalytic cycle for all 3*d* dopants is the stage of “dopant cleaning” with the restoration of its catalytic activity by the beginning of each next hydrogenation cycle. The energy barriers of the rate-limiting step for Ni are the lowest, and the catalytic activity of the dopant decreases with decreasing atomic number L.

The reported R&Ds made it possible to reveal the features of hydrogen s/d behavior of the studied objects, to perform a purposeful search for advanced Mg-based hydrogen storage materials, as well as to develop devices with improved hydrogen storage performances. The obtained results were ranked high by both The Federal Service for Intellectual Property and The American Chemical Society.

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Hydrogen storage materials on the basis of Ti–Fe alloys: state-of-the art and perspectives

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Development of safe and efficient methods of hydrogen storage is one of key problems of hydrogen energy. The methods used at present (high-pressure gas and cryogenic liquid) require compliance with special safety measures, use of hydrogen-neutral design materials and are highly energy consuming. The most compact and safe method for medium-scale hydrogen storage systems is the metal hydride one. However, its implementation is hindered by the high cost of hydride-forming alloys.

The alloys based on TiFe intermetallic can potentially be in 3–5 times cheaper (per unit weight of the stored H_2) than the AB_5- and AB_2-type hydrogen storage alloys conventionally used for hydrogen storage applications due to their favorable hydrogen sorption performances. However, inexpensive methods of improvement of the activation performance, hydrogenation/dehydrogenation kinetics and poisoning tolerance of TiFe are necessary to be developed first.

Though hydrogen systems with TiFe intermetallic and its derivatives were studied for more than 50 years, looking the ways for increase of tolerance of their hydrogen sorption characteristics towards “poisoning” with oxygen-containing impurities in the gas and solid phases has recently gained a special attention. It is confirmed by the analysis of Scopus bibliographic database using keywords “TiFe” and “Hydrogen”: of 357 relevant publications for 1972-2023, 125 (35%) were published since 2018.

This presentation analyses results of studies of preparation routes, phase-structural, morphological, surface and hydrogen sorption characteristics of TiFe-based hydrogen storage alloys reported by various research teams including the early [1,2] and recent (e.g., [3-6]) publications.

It was shown that the improvement of hydrogen sorption characteristics of the TiFe-based alloys can be achieved by:

- Doping the base alloy with metallic additives, first of all, Mn and V. The maximum positive effect which includes preserving high hydrogen sorption capacity, merging two plateau segments on the pressure – composition isotherm, facilitating the activation, improvements of H absorption/desorption kinetics and poisoning tolerance, is achieved by introducing several transition metals which substitute both titanium (A=Zr, Hf) and iron (B=Mn, Ni, Cr, Co, V), at the stoichiometric ratio (Ti+A)/(Fe+B)=1.05–1.1. Addition of the minor amounts (up to 3 at.%) of the rare-earth deoxidizers also improves hydrogen sorption characteristics.
- Controlled introducing of small (below 0.2 wt.%) additives of oxygen into alloy which results in the softening activation conditions and kinetic improvements.
- Surface modification of the TiFe-based alloy by metal nanoparticles (Ni, Pd) catalyzing dissociative chemisorption of H_2.
- Development of composite materials on the basis of Ti–Fe alloys which contain nanoscale carbon taken alone or as a carrier of the catalytic metal nanoparticles mentioned above.

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(Bi)Metallic amidoboranes – synthesis, characterisation and perspective for hydrogen storage

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Metallic and bimetallic amidoboranes can be easily synthesized by liquidless mechanochemical technique. By using the mechanical ball milling technique, solventless solid state reaction between ammonia borane (NH_3BH_3, AB), alkali metal hydrides (NaH, LiH) and alkaline earth metal hydrides (CaH_2 and MgH_2) is absolutely possible [1-3].

Using the Raman spectroscopy for solid state operando monitoring of reaction between ammonia borane and hydrides we sucessfully synthesized two monometallic ($NaNH_2BH_3$, $LiNH_2BH_3$) and four bimetallic amidoboranes ($Na_2Mg(NH_2BH_3)_4$, $Li_2Mg(NH_2BH_3)_4$, $Na_2Ca(NH_2BH_3)_4$ and $Li_2Ca(NH_2BH_3)_4$. As a milling equipment we used PMMA (plexiglass) jars and stainless steel balls. Mentioned approach allowed real time observation of key intermediate phases and a straightforward follow-up of the reaction course. Detailed analysis of time-dependent spectra revealed a two-step mechanism through formation of $MNH_2BH_3{\cdot}NH_3BH_3$ adducts as key intermediate phases which further reacted with MgH_2, giving $M_2Mg(NH_2BH_3)_4$ as final products (M are Li or Na) [1]. We have also developed a new green and rapid mechanochemical procedure for the synthesis of Ca-containing alkaline metal amidoboranes [2], $Na_2Ca(NH_2BH_3)_4$ and $Li_2Ca(NH_2BH_3)_4$, using a similar approach. Also, the tandem technique - operando X-Ray diffraction with temperature profile measurement was used for monitoring of mechanochemical syntheses. On such a way we revealed how the course of the reactions and their thermal profiles strongly depend on the starting alkali metal hydride. For instance, NaH induced a sudden and dramatic increase in temperature of the reaction mixture (sometimes followed by explosion), which induced a partial or total decomposition of thermally labile AB+NaH system and influenced the yield and composition of reaction products. The changing of milling reactor material from insulating plastics (PMMA) to thermally conductive stainless steel readily amended this issue (through more effective heat dissipation). In summary, solid state stainless steel equipment for bimetallic amidoborane synthesis is shown in Figure 1.

In all cases, as a products, only mixed metal amidoborane and hydrogen gas are obtained, without usage of any solvent, fulfilling all aspects of green chemistry.

Having in mind all the problems with rehydrogenation and practical irreversibility of metallic amidoboranes (only indirect rehydrogenation is possible by using the hydrazine [4]), there is only one question - are these compounds very prominent materials for solid state hydrogen storage?

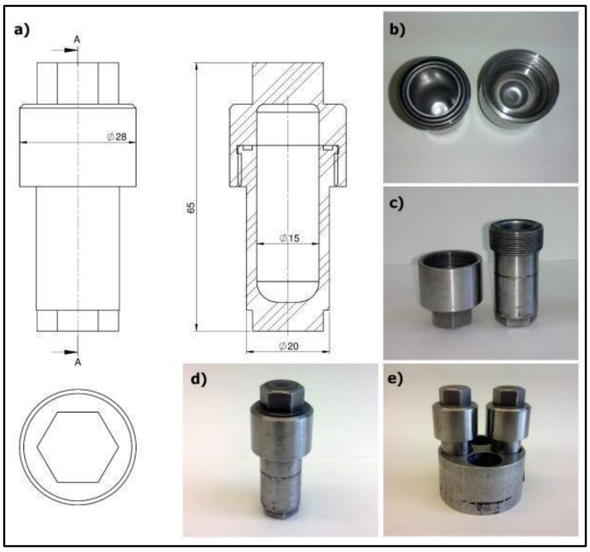

Figure 1. Stainless steel synthesis equipment: a) technical drawing; b) interior of the jar; c) opened jar prepared for sample loading; d) closed jar; e) two jars in sample holder prepared for mounting on the mill.

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Metal hydride H_2 storage and compression units with low suction pressure

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Development of metal hydride (MH) hydrogen storage and compression systems with the low H_2 suction pressure is necessary for the utilization of H_2 produced using high temperature solid oxide electrolyzers and normally released at the pressure close to the atmospheric one. It also gives an opportunity to utilize the low-pressure hydrogen byproduct from chemical industries including chlorine production.

To achieve a reasonably high H_2 absorption productivity, the pressure driving force, i.e., the difference between the operating pressure (1 atm) and the H_2 equilibrium pressure at the cooling temperature for the used MH, should be as high as possible. At the same time, the MH should provide sufficiently high H_2 discharge pressure (at least, 2–5 atm) when heated up to a reasonable temperature, from 90˚C (provided by solar collectors) to 150˚C (low-grade industrial steam).

The most suitable hydride-forming materials which satisfy these requirements are AB_5-type intermetallics on the basis of $LaNi_5$ where Ni is substituted with elements (Al, Mn, Co, etc.) increasing the thermal stability of the intermetallic hydride as compared to $LaNi_5H_x$. Such intermetallics can be easily activated, and their H sorption characteristics are less sensitive to the impurities in H_2 (first of all, water vapors) than for the Ti based AB and AB_2-type hydrogen storage alloys [1].

This work presents results of activities of the co-authors representing FRC PCP&MC RAS (Russia) and HySA Systems (South Africa) on the development of systems able to absorb low-pressure H_2 and to further desorb it at the higher pressures.

The studies of the Russian team were focused on the $LaNi_{5-x}Al_x$ intermetallics (x=0.2–0.8). It was shown that the optimum for the application alloy composition corresponds to x=0.55 allowing to absorb 1.2 wt.% H at T=20˚C and P≤1 atm already after the first activation cycle (vacuum heating to 90˚C) and to desorb up to 1 wt.% H at P≥2 atm and T=90˚C. Further developed low-pressure hydrogen storage and compression unit (1.2 Nm^3 H_2 in the capacity) comprised of the MH powder loaded in cylindrical containment equipped with the internal and external heat exchangers. 9 kg of the $LaNi_{4.45}Al_{0.55}$ alloy powder was mixed with 1 wt.% of the earlier developed [2] graphene-like material doped by catalytic Ni nanoparticles (Ni/GLM). The use of the Ni/GLM catalyst allows to improve H_2 absorption/desorption kinetics, to increase effective thermal conductivity of the MH bed and to prevent agglomeration of the MH particles [3].

The developed unit providing H_2 absorption at ≤1 atm when cooled to 10–20°C with cold water and H_2 release at a pressure above 2 atm when heated to 70–90°C with hot water was successfully tested in integration with a solid oxide electrolyzer and showed high performance.

Further studies carried out at HySA Systems in South Africa showed feasibility of the use in the target application of a standard AB_5-type battery alloy (A=Mm, B=Ni+Co+Mn+Al). This alloy has hydrogen sorption performance close to the one for $LaNi_{4.45}Al_{0.55}$ and can provide reversible hydrogen storage capacity about 1 wt.%H during the operation at T=15–75˚C and hydrogen pressures from ≤1 to ≥2 atm. 8 kg of the AB_5 alloy powder mixed with 1 wt.% of expanded natural graphite (ENG) was loaded into a standard HySA Systems MH container for hydrogen storage and compression (2.68 dm^3 in the inner volume) also comprising inner and outer heat exchangers.

Results of the tests have shown that the total hydrogen capacity of the MH unit exceeds 1 Nm^3 of which about 0.85 Nm^3 are absorbed at the pressure below 1 atm during cooling of the container with running water at T=16–18˚C. About 80% of the low-pressure hydrogen (0.67 Nm^3) absorbs in 30 minutes with maximum flow rate of 30 NL/min. Further heating of the container by steam (T~120˚C) results in the desorption of hydrogen at higher pressures; in doing so, about 0.65 Nm^3 H_2 is desorbed from the unit at the pressure above 5 bar and flow rate of 10–30 NL/min.

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Novel High-Pressure Metal Hydride Container for Hydrogen Compression

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Ti based AB_2 - type metal hydrides are promising materials for hydrogen compression due to the high reversible capacity, and easily adjustable plateau pressure by metallic substitution and excellent cycle life. It has been shown that Ti–V–Mn based alloys, with C14 Laves and BCC phases, possess promising hydrogen absorption capacities with fast absorption/desorption kinetics at ambient temperatures. In particular, a $Ti_{0.5}V_{0.5}Mn$~2 alloy has shown good potential as a metal hydride to be used as part of a hydrogen compression system, with a reversible capacity of 1.9 wt.% at 260 K under H_2 pressure up to 350 bar and a plateau pressure which can be influenced by V substitutions [1].

In the current study a multicomponent C14 Ti – based AB_2 intermetallic (proprietary recipe of HySA systems) was used in a high pressure metal hydride container. Figure 1(a) presents the isotherms of hydrogen absorption at T=20˚C and hydrogen desorption at T=150˚C. The isotherms were calculated on the basis of fitting the experimental PCT data for this alloy taken in the range T= –20…+20˚C, P=0.1…200 bar, using the model of phase equilibria in hydrogen–metal systems which allows for the realistic extrapolation of the results outside pressure–temperature ranges where the experimental data were collected [2]. As it can be seen, this alloy allows for hydrogen compression from PL=100 bar (TL=20˚C) to PH=500 bar (TH=150˚C) with cycle productivity ΔC=115 NL/kg.

Figure 1(b) illustrates hydrogen discharge performance (backpressure regulator setpoint of 500 bar) of a prototype composite metal hydride container for high-pressure hydrogen compression developed by HySA Systems and its industrial partner [3]. The container filled with 0.86 kg of the C14-AB2 intermetallic mentioned above and charged with hydrogen at P(H2)=100 bar and T=10–15˚C was heated to T=150˚C with steam supplied to the inner heat exchanger of the container. It is seen that the increase of pressure (P) in the container begins after 2 minutes from starting steam supply, and after 6.5 minutes it reaches backpressure setpoint accompanied by the start of hydrogen release at P=500 bar. The hydrogen flow rate measured at the exit of the backpressure regulator quickly increases to ~20 NL/min followed by the gradual decrease to zero during ~25 minutes from start of the heating. During the operation in high-pressure H2 discharge mode, the temperature of container wall (carbon fibre wrapping), T(wall), does not exceed 100˚C while the steam temperature at the input (T(in)) and output (T(out)) of the container's heat exchanger is close to 150˚C. The amount of hydrogen desorbed at P=500 bar was of 86 NL, or 75% of the theoretical/equilibrium cycle productivity (see Figure 1(a))

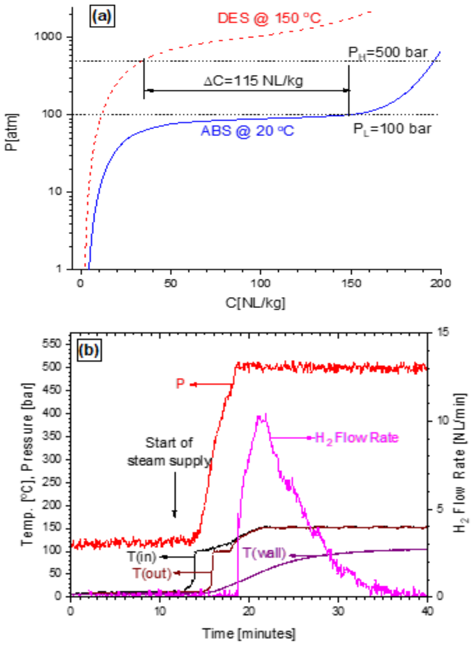

Figure: 1 (a) isotherms of hydrogen absorption at T=20˚C and hydrogen desorption at T=150˚C for C14-AB2 intermetallic (A=Ti+Zr, B= Cr+Fe+Mn+Ni), (b) hydrogen discharge performance of a prototype composite metal hydride container for high-pressure hydrogen compression.

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Hydrogen storage properties of Mg-Ni-Al-V-Ti alloy prepared via ball milling

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The high-entropy alloys are of high research interest in materials science due to their potential as hydrogen storage materials and other promising properties. In their development, the classical alloys which are based on a base metal with added alloying elements, are replaced by a nearly equimolar multicomponent alloys. Mg-based high-entropy alloys with some other capable to store hydrogen alloys or metals with high catalytic activity or better corrosion resistance is a way to improve the performance of magnesium materials as hydrogen storage media and anodes in NiMH batteries. A review and summarized results of high entropy alloys with application as hydrogen storage materials were published recently [1]. Some results about the effect of high entropy alloys on the hydrogen sorption properties of MgH_2 are published also [2, 3]. The 90 wt% MgH_2-10 wt.% CrFeCoNi or CrMnFeCoNi and 95 wt% MgH_2- 5 wt% FeCoNiCrMn high entropy alloys exhibited good cycling performance of hydrogenation/dehydrogenation and enhanced hydrogen storage properties of MgH_2.

More investigations on hydrogen storage properties of high entropy alloys and nanostructured Mg-based alloys regarding synthesis methods, higher storage capacity, fast absorption/ desorption kinetics at lower pressure and temperatures are needed. Driven by these reasons, in the present work the corresponding mixture with composition $Mg_{50}Ni_{12.5}Al_{12.5}V_{12.5}Ti_{12.5}$ is synthesized by ball milling and its hydrogen storage properties are studied at different temperatures.

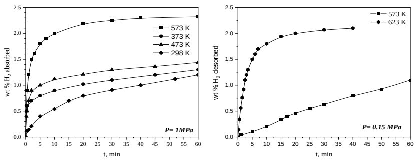

Figure 1. Hydrogen absorption and desorption curves at different temperatues.

The mixture of metals with composition $Mg_{50}Ni_{12.5}Al_{12.5}V_{12.5}Ti_{12.5}$ is milled under Ar in a planetary mill Pulverisette 6 Fritsch with rotation speed 300 rpm, stainless steel balls to powder weight ration 15:1 for duration of 100h. After milling of 10, 20, 40, 60, 80 and 100h some amount of the powder is taken for XRD analyses by using Powder X-ray Diffractometer Bruker D8 Advance with a LynxEye detector. The hydrogen sorption properties are studied at different temperatures 298, 373, 473 and 573 K and a pressure of 1 MPa for absorption and 0.15 MPa and 573 and 623 K for desorption using a Sieverts type apparatus. After 100 h of ball milling under Ar and hydrogenation at 473 K and 1 MPa, the samples are characterized by TEM HR STEM JEOL JEM 2100 with GATAN Orius 832 SC1000 CCD Camera.

The XRD patterns of ball milled for 100 hours under argon of $Mg_{50}Ni_{12.5}Al_{12.5}V_{12.5}Ti_{12.5}$ showed Mg, Al, Ni, V and Ti. TEM analyses confirmed the XRD results. In Fig. 1 hydrogen absorption and desorption curves at different temperatures are presented. Even at room temperatures the kinetics and capacity are good. Of cause at 573 K and 1 MPa the capacity is with highest value of 2.3 wt% and at 298 K is 1.2 wt%. The desorption reaction is not so fast and for 1h at 573 K the desorption capacity is 1.1 wt%, but at 623 K for the same time is 2.1 wt%.

The reversible hydrogen storage capacity of the $Mg_{50}Ni_{12.5}Al_{12.5}V_{12.5}Ti_{12.5}$ is due mainly to Mg and at 573 K is 2.3 wt%. This metallic powder showed fast absorption kinetics and resistance to oxidation. It appears that the effects of ball milling like decreasing particles size and introducing many defects also contributed to these good absorption kinetics properties.

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Kinetic behavior of MgH_2-transition metal composites: towards hydrogen storage

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Hydrogen as an energy vector represents great potential, due to its high gravimetric density and low mass, as well as the fact that combustion does not emit harmful chemical byproducts. Hydrogen has the highest energy density per unit mass compared to any other fuel but a rather low energy density per unit volume. Further, hydrogen storage is a key technology for developing a hydrogen and fuel cell-based economy [1]. Metal hydrides as alternative hydrogen carriers have a wide range of performance parameters such as operating temperature, sorption kinetics, activation conditions, cyclic options, and equilibrium hydrogen pressure. These parameters can be improved or adjusted to meet the technical requirements of different applications. The most commonly used method for hydride destabilization is nanostructuring by mechanical milling which leads to a reduction in the particle and crystallite size of the MgH_2 powder. Nanostructuring is often combined with catalyst addition and composite formation [2,3]. The most of research is focused on the morphological, structural, and thermodynamic effects typical for long milling times, while in this work we have followed the changes taking place under short milling times. The thermal stability of magnesium hydride is related to - changes in the crystallites and powder particle size. The analysis also considered the changes in activation energy. MgH_2-M composites were prepared by mechanical milling of the as-received MgH_2 powder (Alfa Aesar, 98% purity) with the addition of 2 and 5 wt.% of M (M= V, W, Mo). Mechanical milling was performed in s SPEX 5100 Mixer Mill using 8mm diameter milling ball. Samples were milled for 15-45 minutes under the inert atmosphere of argon and a ball-to-powder ratio 10:1 Figure 1. shows the kinetic curves obtained for composites with 5wt% of vanadium. To investigate the desorption process in detail, different models of solid-state kinetics were used as implemented in the code developed in our group. The rate-limiting step of the desorption reaction was determined using the iso-conversional kinetic method due to better accuracy of obtained apparent activation energies. As shown in Table 1 a decrease in apparent activation energies has been observed. It is obvious that the sorption kinetics is affected by material preparation because the reactivity of magnesium with hydrogen is strongly modified by changes in several surface parameters that govern the chemisorption, the dissociation of molecular hydrogen, and hydride nucleation.

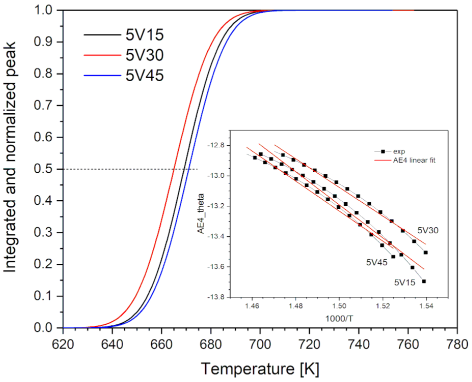

Figure 1. Kinetic curve for MgH_2-5% V nanocomposites mechanically milled for 15, 30 and 45 minutes. Inserted figure: From $\ln g(\theta) = f(1/T)$ the best fit of experimental data is obtained for nucleation.

Table 1. Thermodynamics and kinetics parameters of MgH2-V composites

Sample	HT (°C)	E_{app} (kJ/mol)	VHT (°C)	E_{ACT} (kJ/mol)
5V15	396.12(6)	90(1)	469.9(6)	60.3(2)
5V30	392.01(4)	78(1)	452.4(7)	61.5(7)
5V45	398.03(4)	82(1)	-	-

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Development of a design tool for a metal hydride based hydrogen storage system for underwater applications

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Hydrogen molecules reacts with various metals and alloys under a specific temperature and pressure to form metal hydrides to store hydrogen in the solid phase. Among different types of hydrogen storage techniques, such as pressurized and liquified hydrogen storage, metal hydride storage has the highest volumetric density, i.e., they occupy less volume to store the same amount of hydrogen. Although metal hydrides are advantageous in terms of occupying less volume compared to other storage techniques, their gravimetric density is lower than pressurized and liquified hydrogen storage. Despite this disadvantage, metal hydride-based hydrogen storage is frequently preferred as a hydrogen source in PEM fuel cell applications, especially for underwater applications the ballast weight required for diving is high. For underwater applications, the criteria for selecting metal hydride material should be volumetric hydrogen storage capacity, rate of absorption and desorption, recharging temperature and pressure, the cold start of the vehicle, and cost [1, 2].
This study aims to build a design tool for a metal hydride-based hydrogen storage tank. The design tool will address the use of metal hydrides for underwater applications.

The design tool develops a preliminary system design based on the material and system properties and then produces an initial estimate of the mass and volume of the storage system. It uses the thermodynamic and transport properties of the metal hydride to calculate the parameters needed to estimate the size of the metal hydride-based hydrogen storage tank. This design tool runs on Macros in MS Excel®.

For the material properties, equilibrium conditions and the limitations of the metal hydride are considered. The van't Hoff equation is employed at the maximum tank pressure to calculate the required equilibrium temperature of the metal hydride. The heat balance of the metal hydride tank is estimated at the storage system's properties. During hydrogen charging, the metal hydride produces a significant heat that must be removed to allow continuous hydrogen uptake. Therefore, cooling tubes should be placed in the system. Temperature profiles develop as the produced heat is removed around each cooling zone, i.e., the heat exchange tube. Moreover, basic cylindrical tank geometry (Type I, Type II, Type III, or Type IV) and material are considered to calculate tank mass and volume.

Using the model described above, the primary inputs and outputs of the design tool have been set and given in Table 1.

Table 1. Primary inputs and outputs of the design tool

INPUTS	Hydrogen storage capacity of the metal hydride
	Thermal conductivity of the metal hydride
	Density of the metal hydride
	Void fraction of the metal hydride
	Enthalpy per mole H2
	Entropy per mole H2
	Moles of H2 produced per mole feed
	Mass of usable H2 available in the tank
	External radius of the coolant tube
	Thickness of the coolant tube
	Maximum operating temperature
	Minimum operating temperature
	Tank material
OUTPUTS	System mass
	System volume
	Outer tank diameter
	Tank length
	Number of coolant tubes
	Total mass of the metal hydride
	Tank mass
	Maximum temperature

Metal hydrides as hydrogen storage materials are a promising technology for underwater applications. The design tool developed provides to predict the main characteristics of a metal hydride storage system such as mass and volume, which are the most critical parameters for a vehicular application. This design tool will be helpful to guide researchers in developing different metal hydride-based storage systems for vehicles.

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FUEL CELLS AND ELECTROLYSERS

Alkaline electrolyser for green hydrogen production: the nickel-based catalyst and separator

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Hydrogen is a fuel that is able to replace fossil fuels unavailable naturally on the earth. However, it must be produced from a renewable source to replace fossil fuels. Hydrogen, also a feedstock for industry, is produced mostly by steam-forming natural gas, resulting in high CO_2 emissions. The fact that global warming is becoming visible and that energy demands must be addressed without releasing carbon dioxide into the atmosphere emphasizes the importance of the world's energy transition. Hydrogen in this energy transition has the potential to meet expectations as an energy carrier. It can be produced by electrolysis of water. Hydrogen production from the water will be possible with large electrolysis systems without carbon dioxide emission from renewable sources. Green hydrogen will have a wide range of uses, such as industry, transportation, heating, and power generation. In the hydrogen roadmap of the European Union, establishing at least 6 GW of renewable hydrogen (green hydrogen) electrolysers until 2024 has been determined as a strategic target [1]. The average investment cost of alkaline electrolysers, whose technology has been known since the 1800s, is 840 USD/kW. It is predicted to be 200 USD/kW in 2050 [2]. It is crucial for governments to develop and advance this technology using their own resources, especially in regard to their strategic objectives to build large-scale electrolysers all over the world. In particular, alkaline electrolysers with known technology are widely used due to the absence of the need for noble metal catalysts.

Anion exchange membrane (AEM) electrolyzers, which require lower electrolyte concentrations, draw attention for large electrolyzer plants due to developing anion exchange membranes. The most crucial parts of alkaline and AEM electrolysers for improving performance and lowering costs are the membrane, electrode, diaphragm and catalyst [2].

Catalysts and electrodes for alkaline electrolytes can be prepared nickel based instead of platinum group metals. Alkaline water electrolysis is an old technology using nickel-based transition metals catalysts. One of the most serious problems in this system is the degradation of the components and electrodes in the concentrated solution[3]. The development of ion-conducting solid electrolyte polymer membranes has received a lot of attention recently in an effort to solve these issues. Nafion®, which is the most used of these materials, is preferred as a membrane due to its thermal, chemical and mechanical stability. Nafion® is currently used in commercial proton exchange membrane (PEM) electrolysers and PEM fuel cells. However, PEM electrolysers have some drawbacks, such as high costs and the requirement to utilize noble metal catalysts[4]. As an alternative to PEMs, alkaline anion exchange membrane (AEM) electrolysers, nickel-based catalysts that do not require noble metal catalysts, are increasing in favour in recent years[5]. Thus, AEM-based systems are promising for large-scale commercial electrolyzers because of their fast electrochemical kinetics, use of non-noble metals, and advantages over PEM systems, including low-cost membranes. The new generation of high-performance, safer and sustainable anion exchange membranes are promising in the future electrolyser technology. Poly(arylene ether sulfone), poly(phenylene oxide), poly(ether sulfone ketone) and poly(vinyl alcohol) functionalized polymers with several quaternary ammoniums were developed and used as AEM materials[6].

In this study, nickel-based anode catalysts and cathode catalysts were prepared. OER effective $Co(OH)_2/Ni(OH)_2$ was prepared in the oxyhydroxide form as the anode catalyst, and HER catalyst was prepared to consist of nickel, copper, zinc and phosphorus as the cathode catalyst. Poly(diphenylmethane-co-diphenyl silane piperidine) ionomer was synthesized for an alkaline electrolyzer, and its ionic conductivity and AEMWE suitability were determined using the polarization technique and EIS technique.

Acknowledgements

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Operando Monitoring and Insights for Hydrogen Production via Electrolysis

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Today, climate change and energy security are among the most important issues in the world [1]. To address the requirements of the global low-carbon transition, pressure is on to develop green hydrogen energy sources for the fast phase-out of fossil-fuel production [2]. Therefore, it is of great interest to develop better green hydrogen systems with low cost, high efficiency, extended durability, and high yield. This requires learning the art of hydrogen evolution, transport, and storage steps. Electrolysis is highly promising method for green hydrogen production yet several challenges need to be overcome. *Operando* techniques can offer in-situ monitoring and real-time observation of water electrolysis including the principles of reaction mechanisms, interfacial properties, structural changes of the active sites, electron and ion transfer, gas and water transport properties, and degradation mechanisms.

The present study provides insight into the current progress in *operando* analysis of electrolysis for hydrogen production. Specifically, we provide an overview of the recent advances in imaging methods of X-ray and neutron radiography, and micro-computed tomography; Infrared, Raman, X-ray absorption, photoelectron and electrochemical impedance spectroscopies (Figure 1). The operational principles of these techniques; temporal, spatial and spectral ranges of their applications; and limitations in monitoring and analyses are discussed in detail as well. In addition, reactions that occur in these systems, mechanisms that are taking place, and resultant system durability are presented. Finally, we recommend future directions in operando characterization for enhancing live monitoring of reactions, transport phenomena, and degradation mechanisms in hydrogen production processes [3].

The presented *operando* techniques can provide answers to clarify the chemical and physical processes occurring and help to develop the next generation of electrolysis devices. The cost of H_2 production from water electrolysis is still prohibitively high (3-7.5 USD/kgH_2) compared to other methods. In this respect, new *operando* techniques can have a significant impact on developing new classes of materials and architectures paving the way for the widespread application of green hydrogen production.

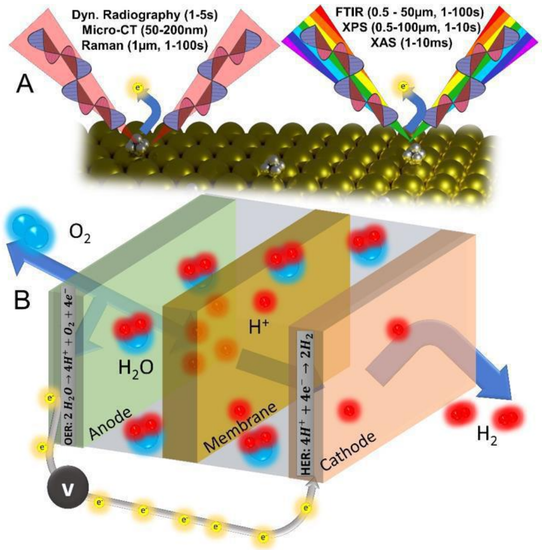

Figure 1. Schematic of artist rendering of (A) *Operando* techniques with their temporal and spatial resolutions. (B) Main electrolysis reactions and a typical system cell structure [3].

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Influence of atomic configuration on popular descriptors for oxygen evolution reaction on complex transition-metal oxide catalysts

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Ruddlesden-Popper (RP) oxides were demonstrated to be promising catalysts for the oxygen evolution reaction (OER) – the most kinetically hindered process in fuel cells and metal-air batteries. These oxides have a general formula of $A_{1+n}B_nO_{3n+1}$, where A is an alkali or alkali earth element, B is a transition metal, and *n* is the number of perovskite layers. The possibility to tune their properties by substituting different elements in the A and B sites makes RP oxides appealing for rational design of low-cost, environmentally friendly, and stable catalysts for OER.

Many studies aim to identify descriptors that can help to predict a catalyst's activity. For instance, in [1] authors performed a statistical analysis of popular descriptors such as O 2*p*-band center, unoccupied 3*d* band center, M−O−M bond angle, and tolerance factor. However, these properties could depend on the distributions of elements in the crystal lattice, especially in such complex oxides as RP, where the interplay between spin, charge, lattice, and orbital degrees of freedom could give peculiar magnetic and electronic structure.

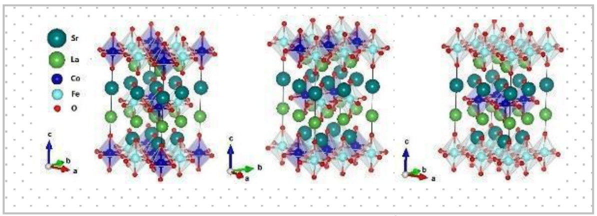

Figure 1. Various relative distributions of cobalt and iron in $LaSrCo_{1/2}Fe_{1/2}O_4$. The left structure is commonly believed to be the most energetically favorable one.The number of Fe-O-Co bridges is maximized in this structure. The number of Fe-O-Co bridges is minimized in the middle structure but there is an equal number of Co and Fe atoms in each layer. The Co and Fe layers interchange in the right structure

To understand how the distribution of elements affects electronic and magnetic properties, we performed density-functional theory (DFT) calculations of $La_{2-x}Sr_xCo_{1/2}Fe_{1/2}O_4$ (see fig. 1) with different distributions of iron and cobalt. Complex transition-metal oxides such as RP and other energy materials present a challenge for DFT calculations due to the strong electron correlation, which leads to the incorrect description of localized *d*- and *f*-electrons by standard DFT approximations. A popular low-cost solution of this problem is to add a Hubbard-like correction *U* to DFT. The value of *U* in general depends on atomic environment, and is therefore challenging to determine. To address this problem, we used ACBN0 exchange-correlation functional [2]. It allows us to calculate *U* self-consistently from first principles. We analyze different configurations of elements in $La_{2-x}Sr_xCo_{1/2}Fe_{1/2}O_4$. We establish that *U* value indeed depends on the local environment of an atom. However, even in the same local environment, *U* could vary by up to 3 eV due to various spin states. We identified a linear correlation between the *U* value and the magnetic moment of the atom. Even in the same spin state and the same local environment U value could still vary in a range of 1.5 eV due to changes in the next nearest neighbors.

We find that the distribution in A-site could also affect magnetic and electronic properties, for example, by changing the spin state of cobalt. The energy of an atomic configuration is found to strongly depend on magnetic and charge orderings. For the same Sr concentration, the most favorable spin state of Co is also found to strongly depend on the distribution of elements in both A and B sublattices. As a consequence, descriptor values such as *d*-band center, transition metals' band overlap, hybridization of transition metal 3*d* and oxygen 2*p* orbitals, and *d*-band center relative to O 2*p*-band center also depend on the distribution of elements. However, the average value of these descriptors for all possible configurations reproduces the trend given by the most energetically favorable structures in $La_{2-x}Sr_xCo_{1/2}Fe_{1/2}O_4$ series.

Acknowledgements

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Fabrication of Ordered Mesoporous Nickel Oxide Based Thin Film Electrodes and Their Electrochemical Properties

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Mesoporous nickel oxide is a p-type semiconductor that finds its application in various fields like lithium-ion batteries, solar cells, energy storage, water splitting, and electronic device[1]. Those applications require high surface area and thin films. There are plenty of methods to synthesize mesoporous nickel oxide and nickel oxide nanoparticles, like sol-gel, electrodeposition, microwave synthesis, etc.[1].

In this work, the molten-salt-assisted self-assembly (MASA) method was adopted to synthesize mesoporous nickel oxide (m-NiO) and nickel manganese oxide (m-$Ni_xMn_{1-x}O$)[2].

Both m-NiO and m-$Ni_xMn_{1-x}O$ thin film electrodes were fabricated by spin-coating clear ethanol solutions of nickel and manganese salts with two surfactants (cetyltrimethylammonium bromide, CTAB, and 10 lauryl ether, $C_{12}E_{10}$) on top of FTO substrates, followed by calcination at high temperatures to ensure formation of the mesoporous oxide.

The thin films were analyzed in a wide range of salt-to-surfactant mole ratio, manganese salt-to-nickel salt mole ratio, and characterized by using powder x-ray diffraction (PXRD), N_2 - adsorption desorption measurement, x-ray photoelectron spectroscopy (XPS), imaging techniques (SEM and TEM) and electrochemical analysis.

The N_2 - adsorption desorption measurement gives a typical type IV isotherm that is characteristic for mesoporous materials. The surface area of m-NiO and m-$Ni_{0.5}Mn_{0.5}O$, calcined at 350 ºC can reach up to 164 m^2/g and 191 m^2/g, respectively. Analysis of XRD pattern gives 3-4 nm crystalline pore walls for both oxides and in good agreement with surface area analysis.

Both mesoporous nickel oxide and manganese nickel oxide electrodes display promising electrocatalytic activity towards oxygen evolution reaction (OER), and have an overpotential of 298 and 223 mV, respectively, at 1 mA/cm^2.

During chronopotentiometry (CP) and cyclic voltammetry (CV) experiments, the very top surface of NiO pore wall transforms to $Ni(OH)_2$ that in the reverse cycle, transforms to NiOOH, and these two species are active in the water oxidation process[3]. The electrochemical cell is represented in Figure 1. Addition of manganese stabilizes the $Ni(OH)_2$ transformation on top of NiO core and improves the overpotential values.

The galvanostatic charge discharge (GCD) experiment show that NiO has high specific capacitance of 140 mF/cm^2 at 0.1 mA/cm^2 current density.

Moreover, due to unique optical properties, NiO shows electrochromic behavior with cycling, and salt-surfactant liquid crystalline gel electrolyte can be used to create an electrochromic device (see Figure 2). The contrast between transparent and dark states can be monitored by changing humidity, calcination temperature, and thickness of the film.

Figure 1.Three electrode electrochemical cell for m-NiO analysis.

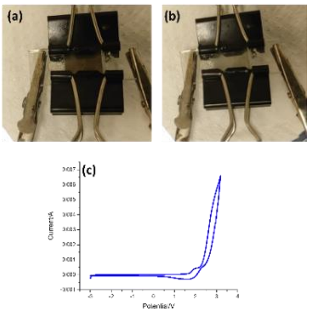

Figure 2. (a) The dark (b) and bleached states of m-NiO electrode, (c) CV of m-NiO-350 electrode from two electrode cell.

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Development of hydroxide ion conducting ionic liquids for non-humidified intermediate temperature alkaline-type fuel cells

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The Emission of greenhouse gases due to a large consumption of fossil fuels is causing serious environmental problems on a global scale. To solve those problems, efforts are being made to utilize renewable energy and to realize more efficient energy conversion. Fuel cells using hydrogen or hydrogen carriers such as methanol as a fuel have attracted much attention as promising devices to realize low carbon energy conversion. In fact, more than 200,000 residential polymer electrolyte fuel cells (PEFCs) have been installed in Japan. This movement is extending to vehicles, and fuel cell vehicles such as Toyota's MIRAI have been already commercialized. However, the electrolyte membranes used in the PEFCs require water to retain high proton conductivity, which limits the operating temperature of PEFCs below 80 °C although the electrochemical activity of catalysts used for oxygen cathode and hydrogen anode increase with increasing the temperature. The higher temperature operation of PEFCs is required also from the viewpoint of more effective use of waste heat as well as lowring the posoning of catalysts with carbon monooxide included in fuel gases. Therefore, new electrolyte materials, which can be used at higher temperatures than 100 °C (intermediate temperature), are being required. We have reported that H$^+$-conduciting ionic liquids (ILs) and their mixtures with phosphoric acid work as promising electrolytes for intermediate temperature operation of fuel cells [1-3]. However, platinum (Pt) catalyst is still required in this series of H$^+$-conducting electrolytes similarly with the currently-used PEFCs because of strongly acidic conditions. To accelerate the wider use of fuel cells, it is necessary to reduce the expensive Pt amount. In this study, we developed OH$^-$-conducting ILs and evaluated them as new electrolytes to realize low- or non-Pt operation of intermediate temperature fuel cells. 1-butyl-3-methylimidazolium hydroxide (BMImOH) was syntheized as an OH$^-$-conducting IL and used as an intermediate temperature electrolyte by mixing with 1-butyl-3-methylimidazolium bis(trifluoromrthanesulfonyl)imide (BMImTFSI) Figure. 1 shows the oxygen reudction reaction (ORR) activity of Pt and glassy carbon (GC) electrodes in the mixed IL under oxygen atmosphere at 30°C and 120 °C. A clear reduction current of ORR was observed for Pt electrode in BMImOH/BMImTFSI = 1/7 mixture although no reduction current was observed in the 1/1 mixture. This difference is due the higher oxygen soubility by the higher molar ratio of BMImTFSI that includes TFSI$^-$ anion with high affinity to oxygen. With increasing the temperature from 30°C to 120 °C, both positive shift of onset potential and increase in the current density of ORR were observed. Interestingly, the similar tendency with the better ORR activity was observed for GC electrode, suggesting the possibility to use inexpensive carbon materials as electrode catalysts. However, the onset potential should be more positive for the practical use. The ORR activity of catalysts is strongly affected by the adsorption of ionic species [4], and BMIm$^+$ cation is considered to adsorb easily on the surface of catalysts because of its planar structure. Therefore, tetrabutylphosphonium hydroxide (TBPOH) with a bulky TBP$^+$ cation was applied as OH$^-$-conducting IL to achieve the better ORR activity. Its details will be also reported.

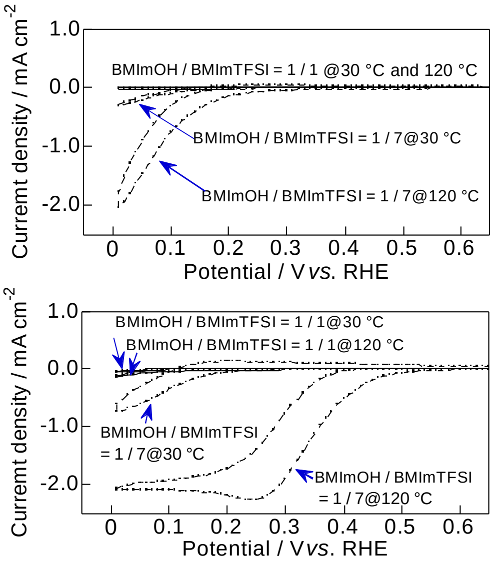

Figure 1. Cyclic voltammograms of (a) Pt and (b) GC electrodes in O$_2$-saturated OH$^-$-conducting ionic liquids.

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Electrode development for nitrate reduction and ammonia production with Lithium mediated materials

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Ammonia is primarily manufactured by the century-old Haber-Bosch process, which runs at high temperature and high pressure. It is regarded as an important feedstock. In contrast, the electrochemical nitrogen reduction reaction (eNRR) has significant potential as a replacement for the Haber-Bosch process because it can produce ammonia at ambient conditions. Low Faradaic efficiency and a slow production rate, however, make it difficult to employ practically. Lithium-mediated eNRR has recently attracted considerable interest because of its outstanding performance and reproducibility. The inadequate understanding of the system's functioning, however, limits further advancement.

Here, we show that two chemical processes—dinitrogen splitting and protonation to ammonia—followed the electrochemical deposition of lithium to initiate the lithium-mediated eNRR.

Firstly, CeO_2 synthesis was performed in Ultra spray pyrolysis device. In the experiment carried out at high temperature (700°C), nano-sized powder material synthesis was performed. Then, by adding Lithium in different ratios (2-4-8-10%), material synthesis was carried out under the same conditions.
For electrochemical activity studies, electrodes were formed on glassy carbon with synthesized materials and nitrate reduction studies were carried out in neutral environment and H-Cell.
The characterization tests of the synthesized materials were completed. The results were compared with XRD, BET, SEM, FTIR tests. The solutions prepared by the indiphenol blue method were compared with the UV test and the amount of ammonia formation was tried to be determined.

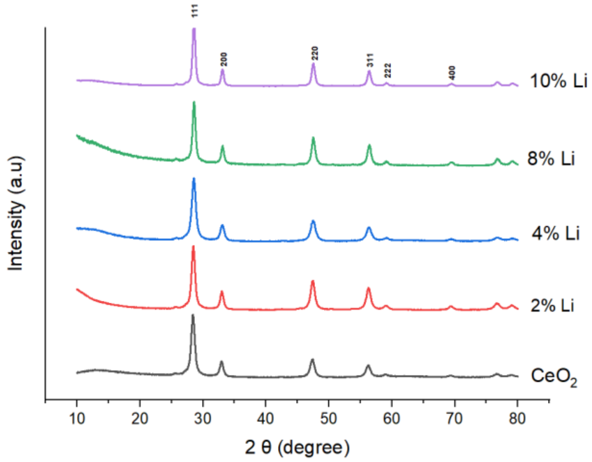

Figure 1. The histogram of XRD illustrating pure CeO2 and different concentration of Lithium added to CeO2 powder synthesis crystallographic orientations

According to the XRD results, as the lithium contribution is increased, the main peak shift is observed. It is observed that the CeO_2 character begins to change with the lithium effect.

Acknowledgements

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Effect of porosity-graded (La,Sr)FeO$_3$ –(Ce,Sm)O$_2$ electrodes on the long-term performance of solid oxide electrolysis cell

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Solid oxide electrolysis cells (SOECs) are considered good candidates for clean energy generation and provide ~92% electricity-to-fuel efficiency [1]. However, SOECs exhibit poor performance and long-term performance degradation. The main reason for the poor SOEC performance is the shortness of triple-phase boundaries (TPBs) where oxygen evolution reaction takes place at the anode. Time-dependent performance degradation originates mostly from high oxygen partial pressure build-up at the electrode/electrolyte interface and thus, delamination. Several electrocatalyst/ionic conductor composite electrodes such as (La,Sr)FeO$_3$-(Ce,Sm)O$_2$ (LSF-SDC) have been intensively investigated recently due to its high electrical conductivity. To maximize TPB length, researchers proposed to produce nanostructured electrocatalyst/ionic conductor composite anodes by means of depositing an ethylene glycol (EG)–based polymeric precursor.

Recently, the origin and the means to control the amount of large pores observed in EG-based polymeric precursor-derived electrode structures were determined [2–5]. This enables the fabrication of electrodes with controlled/graded porosity in polymeric precursor-derived electrode films, which could prevent oxygen pressure build up and help achieve stable SOEC air electrodes.

The current study focuses on the contribution of porosity-graded layers at the electrode/electrolyte interface to the time-dependent electrochemical performance of SOEC. To create a functionally graded layer by changing pore size, nitric acid was utilized as a pore former. Porosity-graded LSF-SDC anodes were deposited on YSZ electrolytes by spin coating. As-prepared anodes were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and electrochemical impedance spectroscopy (EIS).

EIS measurements show that long-term electrochemical performance can be improved with a functional layer positioned between the electrode and electrolyte by grading the pore size.

Acknowledgments

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Surface characteristics and advanced electrocatalytic properties of oxophilic metal modified rutile composite supported platinum electrocatalysts

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For the wide-range implementation of polymer electrolyte membrane (PEM) fuel cells, it is most essential to produce low-cost durable units. As the currently used Pt/C electrocatalysts are responsible for 30-40% of the price of the PEM fuel cells, intense research is focused on either replacing Pt with cheaper alternatives or decreasing the Pt load while enhancing the activity and longevity of the catalysts by suitable modification of the support. In our previous studies this concept was realized by synthesizing Pt electrocatalysts supported on a conductive and corrosion resistant composite consisting of oxophilic metal M (M: W, Mo)-doped TiO_2 and various carbonaceous materials [1-2]. In these multifunctional supports the carbon backbone is responsible for the high surface area and electrical conductivity, the TiO_2 component helps in stabilizing the Pt in highly dispersed state thus offering resistance against electrocorrosion, while the dopant metal cations incorporated into the titania improve the conductivity and provide valuable co-catalytic function, thus the composite supports can mitigate the known drawbacks of the current state-of-art Pt/C systems [1-2]. The transition metal dopant facilitates the oxidation of CO at much lower potentials than on pure Pt, which is important when hydrogen from steam reforming is considered as fuel [3]. The aim of the present work is the study of $Ti_{(1-x)}M_xO_2$-C (M: Mo, Sn; x: 0.1-0.3) composite supported Pt electrocatalysts. In this contribution, our efforts were aimed at elucidating the effect of (i) the type of carbonaceous materials, (ii) the mixed oxide/carbon ratio and (iii) the nature of active M-Pt assemblies in mixed oxide-carbon composite supports on the electrocatalytic performance of related Pt catalysts.

The technique previously developed by our research group for Ti-Mo mixed oxide–carbon composite materials [2-3] was adapted for the preparation of tin-containing composites of various compositions. We demonstrated that the composites and Pt electrocatalysts prepared by this modified synthesis route were free of segregated Sn^0 or SnO_2 phases, possessed a more homogeneous/uniform mixed oxide distribution, and the ECSA values were comparable to those obtained on Mo-based composites of similar composition (~60-80 m^2/g_{Pt}). Comparison of Mo- and Sn-containing 20 wt.% $Pt/Ti_{0.8}M_{0.2}O_2$-C electrocatalysts with a high carbon content (75 wt.%) revealed that the Sn-containing catalysts can be not only promising CO-tolerant anode but also cathode catalysts for potential use in PEM fuel cells.

We proved that during the reductive pretreatment of the Mo-containing catalysts, ionic Mo formations appear on the Pt particles, which increases their stability [4-5]. *In situ* XPS study of the effect of reductive treatments of Sn-containing electrocatalysts showed that this treatment induces Sn-Pt alloying. During oxidative treatment, the alloyed particles are encapsulated by a layer of SnO_x layer, but this encapsulation is reversible by repeated reduction.

Integration of novel catalysts into membrane electrode assemblies (MEAs) and building of PEM fuel cells and stacks from these MEAs for performance tests under laboratory conditions and for application in new hydrogen powered electronic devices will be demonstrated in the lecture.

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Innovative electrodes for PEM fuel cells based on graphene materials

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Graphene-enhanced electrode materials have started to be evaluated especially lately for hydrogen storage for improving the performance of proton exchange membrane fuel cell (PEMFC) applications. Graphene is composed of a single layer of graphite, that consists of sp^2-bonded carbon atoms forming a honeycomb or hexagonal type of lattice structure.

The unique chemical and physical properties of graphene and its derivatives (graphene oxide GO, heteroatom-doped graphene, and functionalized graphene) have stimulated tremendous efforts and made significant progress in PEMFC applications. The graphene has large surface area and porosity, excellent electrical conductivity, and interconnected pore structures, not only providing more anchor sites to immobilize metal oxide nanoparticles but also improving the mass transport of reactants.

The system efficiency of fuel cells is significantly higher than the combustion engine, mainly due to the low emission of pollutants as well as the chemical energy of fuels is directly converted to electricity. Therefore, fuel cells are considered as one of the attractive technologies to address global energy and environmental issues and make our lives cleaner and more sustainable. The larger surface area and higher mass activity further reduce the system costs by lowering the catalyst loading. However, the costs of synthesis, storage, and processing of graphene-based materials themselves should be taken into consideration.

Cost is a key factor that influences the manufacturing graphene-based materials for real PEMFC. Metal-free, PGM-free, or low-PGM graphene-based electrocatalysts are regarded as a great opportunity to replace the high-cost Pt/C-based catalysts.

Doped graphene and GO provide many anchoring sites for active metal particles, leading to a uniform dispersion. Moreover, the high surface area and electrical conductivity of graphene-supported catalysts favor various electrochemical reactions, such as ORR, and exhibited a good proton conductivity. For most graphene-based electrocatalysts, their performances were only evaluated in the half-cell test, which cannot accurately represent their activities and durability under practical operating conditions.

One of the main drawbacks of the utilization of graphene for fuel cells is that the graphene sheets tend to restack due to the attractive forces between graphene sheets, leading to a decrease in the availability of active sites.

This work uses the expertise of the Materials for Hydrogen Energy group of ICSI ENERGY to produce a laboratory-based proof of concept: Membrane Electrode Assembly (MEA) as the main component of a fuel cell. The paper presents a protocol to prepare MEA where the hardware components are required to enable effective MEA operation.
This work summarized the progress associated with applications of graphene-based materials in fuel cells. Comparable to the commercial Pt/C catalyst, metal-free heteroatom-doped graphene are evaluated for ORR. Doped graphene, GO, and rGO provide many anchoring sites for active metal particles, making them dispersion uniformly.

Acknowledgments

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Review Study: Possibility of Production of Carbonate Precusors for LCO and NMC Lithium ion batteries from LCO, NMC, and LMO Spent Batteries

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Lately, lithium batteries has dominated the market for their exceptional properties and unique features such as high specific capacity, high specific energy, life span, and stability. However, the materials that make up lithium batteries are not abundant and expensive, the thing that makes a huge obstacle for this technology to take off further smoothly without major problems.To insure a sustainable supply of the raw materials for Li-ion battery industry and particularly cathode active materials, the spent batteries should be recycled to create a sustainable life cycle. In this study, the focus will be on the hydrometallurgical methods, as it is less costy and more controllable.

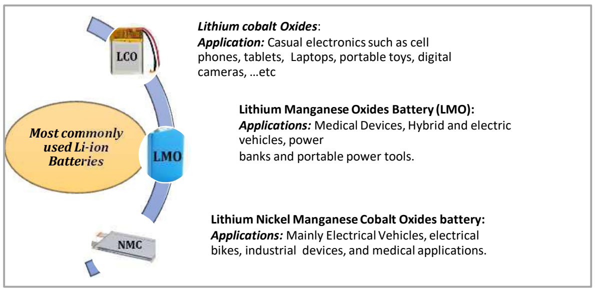
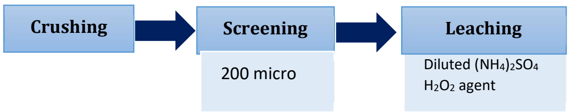
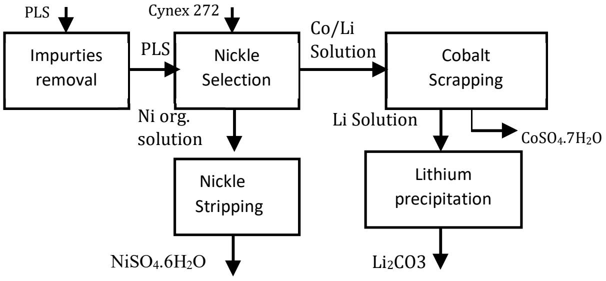


Figure 1. Most commonly used Li-ion batteries

Precious materials recovery: The black mass makes up over 50% of the battery [1]. However, half of the black mass is anode material (i.e. graphite). The spent battery goes through physical process to recover the black mass, subsequently the metals are leached with acidic solution $(NH4)_2SO_4$. Further the precious metal (i.e. Co, Ni, and Li) are selected using hydrometallurgical methods :





The products CoSO4 and NiSO4 are used as a feed for precusors production.

Synthesizing of precusors (Carbonate precusor was selected) [2]: The synthesizing process is descriped in table 1 below:

Raw materials	**NMC source:** $NiSO_4.6H_2O$, $MnSO_4.H_2O$, **and** $CoSO_4.7H_2O$ 8:1:1 **Lithium Source:** $Li2CO_3$ **Solvents:** Deionized water, ethylene glycol. EG:DI ratio is 2:1 **Precipitant:** Ammonium bicarbonate.
Method	Hydro thermal in three stages: NMC mixing (170ºC ± 10/ 12 hr) Calcination (450ºC/ 1hr)Sintering (800ºC/ 10hr) (See Figure 2)
Testing	- XRD - Charge capacity (Voltage cell): Anode: Li Metal Electrolyte: LiPF6 1 M dissolved in EC:DC:DMC 1:1:1

Table 1. Most commonly used Li-ion batteries

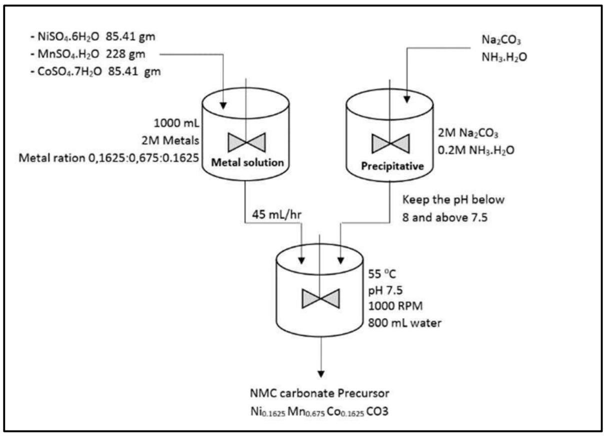


Figure 2. Most commonly used Li-ion batteries

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Nitrogen-doped graphene oxide as innovative catalysts for PEM Fuel Cells

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Proton exchange membrane fuel cells (PEM FCs) are the current focus of the research for FC vehicle applications. Developing a highly efficient catalyst is of great importance for PEMFCs and also for the chemical industry. The main drawbacks for PEMFC are mentioned: the need for improving the performance of the platinum-based catalyst and its poor stability against the load change during FC operation, the acceptable durability of carbon support material, all these leading to increasing of the overall cost of the PEMFC. Nitrogen-doped graphene oxide catalysts with high catalytic performance could be one of the promising long-term solutions for the commercialization challenge of PEMFCs. High performance electrocatalysts for oxygen reduction reaction (ORR), which can replace/reduce rare metals base catalysts are highly desirable for the effective commercial development of PEMFCs. The key to answering this is to determine the contribution of four nitrogen doping configurations, namely pyrrolic nitrogen, pyridinic nitrogen, graphitic nitrogen, and pyridine-nitrogen oxide and to make a correlation to the catalytic performance.

Here we report the obtaining of nitrogen-doped graphene oxide as catalyst for PEMFC, by using a dedicated green-chemistry method in mild reaction conditions. This work uses the expertise of Mat4H group of ICSI ENERGY to produce a laboratory-based technology: a single-step synthesis of nitrogen-doped graphene oxide (N/rGO). The work demonstrates the ability to serve as catalytic material for ORR with the target to identify an inexpensive alternative to platinum-based catalysts for PEM fuel cells.

Nitrogen-doped graphene oxide was synthesized by using a single-step synthesis microwave method in the presence of graphene oxide as the source of carbon and urea as the source of nitrogen, and different reduction agents. The doped-graphene oxide was demonstrated to act as a metal-free electrode with a much better electrocatalytic activity, long-term operation stability, and tolerance to crossover effect than platinum for oxygen reduction *via* a four-electron pathway in fuel cells.

A successful obtaining of N/rGO in a typical small-scale synthesis is proposed by using a green chemistry microwave protocol at a power as low as 80 W in atmospheric pressure. A detailed comparison of physical and chemical properties is presented. The electrocatalytic activity toward the ORR was investigated by specific techniques (Fourier infrared spectroscopy, X-ray spectroscopy measurements, BET specific surface area. The electrocatalytic activity of the synthesized catalysts toward the ORR was investigated by specific techniques, such as cyclic voltammetry, electrochemical impedance spectroscopy and I-V polarization.

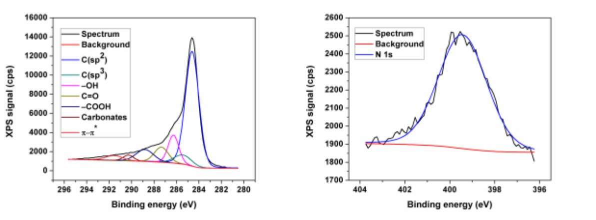

Figure 1. XPS spectra for N/rGO

The work highlights the ability of few-layer N/GO to serve as catalytic material for ORR electrode in the attempt to find an inexpensive alternative to platinum catalysts for use in proton exchange membrane fuel cells. Electrochemical evaluation of N/rGO leads to significant improving of its functional characteristic in particular electrocatalytic activity in oxygen reduction reaction: well-defined cathode peaks for different scan rate and long term stability. N/rGO was obtained with the highest nitrogen concentration of 7 wt%, a high specific surface of 250 m^2 g^{-1}, and a high porosity, which gives the potential as catalytic material.

Acknowledgments

This work was carried out through the Nucleus Program, financed by the Ministry of Education and Research, Romania, project no. PN 23 15 01 03; project PN-III-P2-2.1-PED2021-0840 PED 695/202, and 19PFE/30.12.2021 - Supporting the Change for ICSI – acronym SC-4ICSI, cod 1141/ 114500.

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Development of High Entropy Oxides for Use in Solid Oxide Fuel Cells

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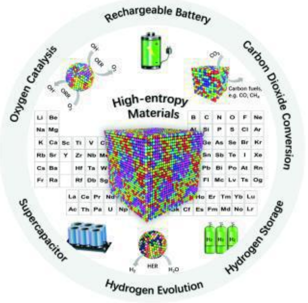
In recent years, energy consumption has been increasing with technological and industrial developments. This leads to the search for clean, efficient, economical, and sustainable energy sources. Among these sources, ceramic-based solid oxide fuel cells, which are considered among the most efficient FCs, draw attention. (Campanari et al., 2016)Solid oxide fuel cell is an electrochemical energy conversion device that converts the chemical energy of the fuel directly into electrical energy, attracting great attention due to its high efficiency, fuel flexibility, and environmental friendliness. However, high operating temperatures (800− 1000 ◦C) cause the cells to be short-lived. Reducing the operating temperatures to 600− 800 ◦C is one of the effective approaches to solving this problem. $La_{0.7}Sr_{0.3}MnO_3$ LSM shows outstanding electronic conductivity, excellent electrocatalytic activity, and good stability for oxygen reduction in the temperature range of 800-1000 °C, but its electrochemical performance is significantly reduced at reduced operating temperature. (Carter et al., 1992; Jiang & Wang, 2005)



In recent years, high entropy oxides have received increasing attention. High entropy oxides usually contain 5 or more elements with small proportions of minor elements and have high mixing entropy. They can be easily synthesized, produced and analyzed. (Oses et al., 2020) ABO3-type perovskite oxide is of interest for solid oxide fuel cells due to its unique dielectric, ferroelectric, pyroelectric properties, and catalyst properties.

Many high entropy oxides have been found to improve thermal characteristics, magnetic properties, catalytic activity, and energy storage and conversion performance, but have less application in solid oxide fuel cells. In this study, the potential application of $La_{0,5}Sr_{0,5}Co_{0,25}Fe_{0,25}Ni_{0,25}Cu_{0,25}O_3$ perovskites in medium temperature solid oxide fuel cells was investigated

LSCFNC powder was synthesized using the sol-gel method. As starting chemicals, nitrates of all of the considered cations were used: $La(NO_3)_3{\cdot}6H_2O$, $Sr(NO_3)_2$, $Co(NO_3)_2{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$.

First, the stoichiometric amount of these nitrates was dissolved in distilled water, then citric acid was added to the solution. The molar ratio of all cations and citric acid in the mixture was 1:2. The solution was heated to 80°C with continuous stirring with the aid of a magnetic stirrer. The resulting gel was dried at 250°C for 2 hours to remove residual organics and nitrates. The dried gel was calcined at 700°C, 900°C, 1100 and 1300°C for 6 hours.

YSZ Synthesis

Yttria-stabilized zirconia (YSZ) with general formula $(ZrO_2)_{1-x}(Y_2O_3)_x$ and $0.08 \le x \le 0.1$, is the most studied electrolyte for SOFCs. The best value of conductivity is obtained for the compound containing 8 mol% of yttrium oxide. In this study, zirconia powders stabilized with 8 mol% yttria were synthesized using the sol-gel process. $ZrO(NO_3)_2.xH_2O$ and $Y(NO_3)_3.6H_2O$ were dissolved in and mixed in ethylene glycol, citric acid, and purified water, respectively. Then, $Y(NO_3)_3.6H_2O$ was added to $ZrO(NO_3)_2.xH_2O$ solution drop by drop and mixed to make YSZ solution. The molar ratio of citric acid to total metal ions (Zr + Y) is 4:1 and CA/EG is 1:1.

After mixing, the temperature was raised to 80°C and the pH was adjusted to 3.6 with HNO_3. The resulting suspension was mixed until homogeneous. This white and milky mixture was dried at 120°C and sintered at 1200°C for 2 hours.

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Development of bolt-microtubular solid oxide fuel cells

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In this study, the effect of anode support thickness on the formability and performance of bolt-microtubular anode supports, for which the geometry has been recently introduced in the literature [1], are investigated. For this purpose, a tape casting slurry of NiO-YSZ (66-34 wt. %) anode support layer was prepared by using proper amounts of dispersant (fish oil), solvent (a mixture of methyl ethyl ketone and ethanol), binder (polyvinyl butyral) and plasticizer (polyethylene glycol). After ball milling and magnetic stirring processes, the slurry was tape cast with 300 µm doctor blade gap. The tape width was adjusted to 10 cm. Following drying under ambient conditions, ~10 cm, ~15 cm and ~25 cm long anode support tapes were cut. These tapes were then wrapped on a threaded rod of M5 class having 5 mm major diameter. After the lamination under 70 MPa pressure for 4 min at 60 °C with an isostatic pressing device, the threaded rod was removed. The bolt-microtubular anode supports were cut by a laser cutting device and fired at 1100 °C for 1h. Next, NiO-YSZ (50-50 wt. %) anode functional layer was dip coated followed by sintering at 1150 °C for 2h. Similarly, YSZ electrolyte, LSM-YSZ (wt. %: 40-60) cathode functional layer and LSM-YSZ (wt. %: 90-10) cathode current collections are dip coated in the given order. The electrolyte layer was sintering at 1400 °C for 4h, while the sintering of both cathode layers were achieved at 1000 °C for 2h. Besides the bolt-microtubular cells (Bs), conventional microtubular anode supports were prepared by using a rod having 5 mm diameter and microtubular cells (Ms) were built on these supports similarly for comparison. The photos of the bolt-microtubular and micortubular cell prepared with ~15 cm long anode support tape are shown in Figure 1.

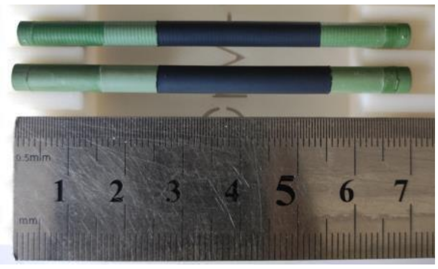

Figure 1. Photo of bolt-microtubular (top) and microtubular cell (bottom)

Physical properties of the cells and anode supports were determined by a stereoscopic microscope (Leica EZ4 W, Leica Microsystems, Germany), while the electrochemical performances of the cells were also measured at 800 °C under 0.3 NL/min hydrogen flow by a fuel cell test station (Arbin Instruments, FCTS, Texas, USA) with external current collection strategy by using a silver wire of 0.5 mm diamater. The structural analyses show that the degree of patterning tends to decrease with increasing the length of anode support tape. The electrochemical performances of bolt-microtubular cells (B1 with ~15 cm and B2 with ~25 cm tape length) and microtubular cells (M1 with ~15 cm and M2 with ~25 cm tape length) are compared in Figure 2. The cells with ~10 cm long anode support tape are broken during the tests due to inadequate support thickness. The results indicate that bolt-microtubular cells overperform conventional ones and the performance improves with the degree of surface patterning due to increased electrochemical reaction zones by enlarging electrolyte-electrode interfaces.

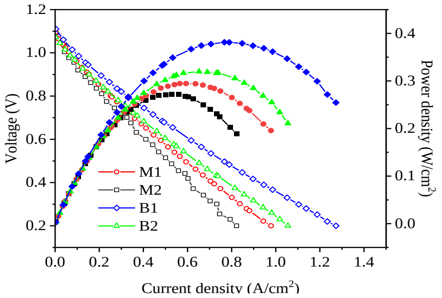

Figure 2. Electrochemical performances of the cells

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Impact of spin coating rates on the surface chemistry and electrochemical performance evolution of (La,Ca)CoO$_3$ solid oxide cell electrodes

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Solid oxide cells (SOCs) can potentially remedy the intermittency problem of solar and wind-based energy conversion systems. For these devices to be commercially available, the long-term performance loss related to changes that occur in their components at relatively high temperatures of 600-800 °C must be mitigated. One such change that causes performance degradation is the segregation of the A-site dopant, Sr^{2+}, at the surfaces of ABO$_3$ –type (La, Sr)CoO$_3$ oxygen electrocatalysts, forming resistive SrO/Sr(OH)$_2$/SrCO$_3$ phases. The root cause of Sr surface segregation has been identified as i) electrostatic attraction between the positively charged oxygen vacancies at the electrocatalyst surface and the negatively charged Sr at the La position and ii) elastic strain caused by the larger Sr^{2+} at the smaller La^{3+} sublattice [1].

Recently, we have attempted to replace Sr^{2+} with Ca^{2+}, which would serve the same purpose of generating additional oxygen vacancies, while minimizing the lattice strain due to the similarity of the cation size of the latter to that of La^{3+}[2]. Our experiments on (La, Ca)CoO$_3$ (LCC) thin film electrodes prepared by liquid precursor deposition revealed that their long-term performance stability depended on surface chemistry evolution, which was determined by the pre-heat treatment temperature [2].

In this work, we investigate whether long-term performance stability of LCC is affected by the fabrication parameters, the rate at which liquid precursor is spun onto the ellectrolyte substrate in this particular case. Figure 1 shows how area specfic resistances of LCC electrodes deposited using different spin coating rates changes upin long-term exposure to 700 °C. Evidently, high spinning speed results in electrodes with higher electrochemical performances that do not change significantly with time. On the other hand, LCC electrodes prepared by higher speed spin coating exhibit poorer initial performance and long-term stability.

Through scanning electron microscopy and x-ray photoelectron spectroscopy studies, it was determined that initial deposition rate determines the amount of surface cracks in the film, which influences the rate at which carbonaceous gases are released during drying. This, in turn, has a significant impact on the surface chemistry evolution, and thus, performance degradation rate.

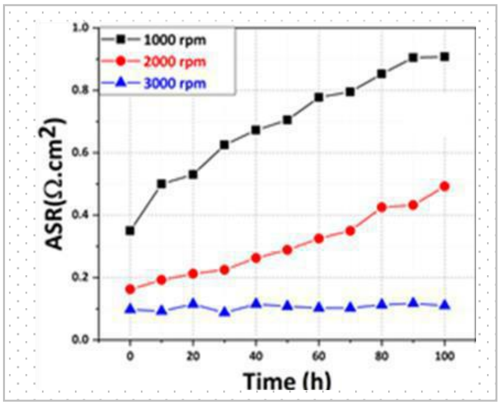

Figure 1. Changes in the area specfic resistances of LCC electrodes deposited using different spin coating rates with time at 700 °C.

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Development of titanium-based porous composites for anode substrates of solid oxide fuel cells

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Solid oxide fuel cells (SOFCs) are an efficient source of electricity for transport, stationary and mobile power stations, which are the main components of hydrogen energetics. At present, the key direction of increasing the efficiency and durability of SOFCs is the reduction of the operating temperature from 800–1000°C to 550–650°C. This can be done by replacing ceramic anode substrates (for example, of NiO–8YSZ system) with porous metallic anode ones. By the way, the thermal expansion coefficient of titanium alloys is in the range of $9\text{-}10\cdot10^{-6}\,^{\circ}C^{-1}$ that is close to the known for anode, electrolyte and cathode ceramic materials in a SOFC.

In this work, the microstructure and physico-mechanical properties of the candidate solid oxide fuel cell anode materials of the Ti–SiC (material 1 with 30% porosity) and TiC–AlON (material 2 with 35% porosity) systems were investigated in the initial state and after holding at 600°C in air or hydrogen. Scanning electron microscopy analysis revealed that the phase composition of material 1 presents titanium carbide TiC and titanium silicide Ti_5Si_3, whereas material 2 presents titanium carbide TiC, aluminum oxynitride AlON and alumina Al_2O_3. It was found that in the initial state flexural strength of materials 1 and 2 is 105 MPa and 110 MPa, respectively, whereas their electrical conductivity is $3.81\cdot10^5$ S/m and $4.88\cdot10^5$ S/m, respectively. At the same time, material 1 is fractured mainly by transgranular cleavage (Fig.1*a*), and material 2 is fractured by transgranular cleavage with some elements of intergranular cleavage (Fig.1*b*).

At 600°C and holding for 3 hours in air, the studied physico-mechanical characteristics of material 1 are 71 MPa and $3.05\cdot10^5$ S/m, while the fracture micromechanism remains the same. Corresponding characteristics of material 2 is 140 MPa and $4.88\cdot10^5$ S/m at the predominance of intergranular fracture of the TiC phase and microductile fracture of aluminum oxynitride AlON. At 600°C and holding for 3 hours in hydrogen, these characteristics of material 1 are 41 MPa and $3.39\cdot10^5$ S/m at significant changes in the fracture micromechanism with the appearance of a large number of intergranular secondary microcracks (Fig.1*c*). For material 2, they are 80 MPa and $4.88\cdot10^5$ S/m at the predominance of intergranular fracture (Fig.1*d*).

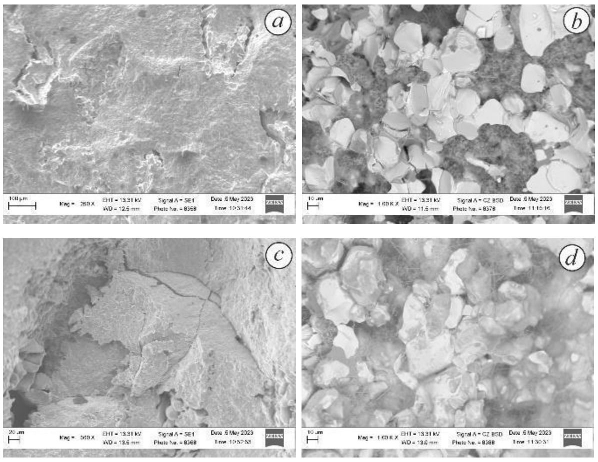

Figure 1. Microfractograms of material 1 (*a*, *c*) and material 2 (*b*, *d*) in the initial state (*a*, *b*) and after holding for 3h in hydrogen at 600°C (*c*, *d*).

Based on the obtained results, it was established that both investigated materials have a high level of electrical conductivity under different test conditions, but in terms of mechanical properties, the composite of the TiC–AlON system has an advantage over the composite of the Ti–SiC system.

Acknowledgements

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The Effect of Nitrogen Coating Pressure on the formation of Macroparticles in TiN thin film coatings

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Fuel cells are systems that produce energy without emitting harmful greenhouse effect gases [1]. The biggest obstacle to the use of fuel cells in civil applications is their cost. One of the important components of the fuel cell is the bi-polar plates [2]. Within the scope of this study, the development of corrosion resistant thin films for metallic bi-polar plates are examined. Bi-polar plates of fuel cells can be produced from various materials such as graphite based, polymer based and metals. Due to its advantages such as formability and machinability, relatively low cost and low gas permeability properties, in this study, thin film coatings on metallic plates preferred and production parameters were studied [3]. Bi-polar plates responsible to the following versatile and imporant tasks in PEMFC. Tasks of bipolar plates[4];

- Keeping fuel cell components compactly together.
- Collecting and transporting electrical charges from the anode side to the cathode side.
- Homogeneus delivery of reactant gases to catalyst coated active surfaces through the flow channels.
- To provide mechanical support for the fuel cell stack to hold together and to withstand the clamping force applied on the stack.
- To transfer the heat relesed during the fuel cell operating process to the outside of the cell.

In addition to being one of the most costly parts with a rate of %45, bi-polar plates make up %80 by mass of a fuel cell [5]. Plates that corrode in a short time due to oxidation and reduction reactions in the PEMFC, working environment should be coated with protective thin films that can remain stable during the working process. Gold (Au), which is preferred due to its chemical stability and conductivity, however, it increases the cost of fuel cells. The main goal is to search for cost-performance efficient coatings on steel plates, which are frequently used in metallic bipolar plates. In this study Titanium (Ti) and Titanium Nitride (TiN) materials are preferred. Various Physical Vapor Deposition (PVD) techniques are used as a coating method. In this study Ti, TiN thin film coatings has been conducted on stainless steel plates with the Cathodic Arc Evaporation (CAE) technique. In order to prevent crack pitting related corrosion over the plate surface, macro and micro particle occurance has to be eliminated.

As can be seen in figure 1, SEM images shows that CAE coating pressure for N_2 and micro particle occurrence is strongly related to each other. Both macro particle size and macro particle count relation is given in figure2.

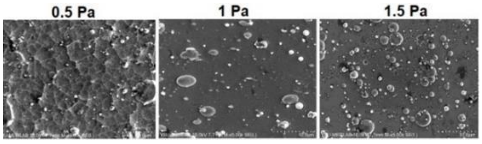

Figure 1. N_2 coating pressure relation with macro particle occurence.

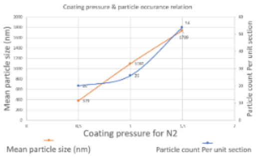

Figure 2. N_2 Coating pressure macro particle relation.

Ti inter layer TiN top layer coated serpentine type air funnel bi-polar plate is shown in figure 3.

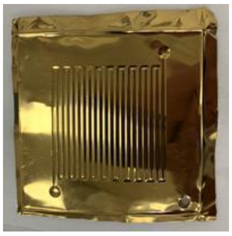

Figure 3. Ti interlayer TiN coated serpentine air funnel BPP.

The present study provides insights into the importance of the coating pressure and macro particle occurrence relation.

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Protective coatings based on CrN for current collector materials of molten carbonate fuel cells

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Bipolar plates and current collectors are critical metallic components for commercial MCFC stacks. In fact for commercial MCFC systems, up to 55 % of the material content could be the metallic hardware (for the complete system) which includes cell, stack, and balance-of-plant materials. The stability in a corrosive carbonate atmosphere at high temperature, good electrical conductivity and low contact resistance with the electrodes are desired characteristics of bipolar plates and current collectors. The bipolar plates are exposed to different atmospheres on the anodic side, cathodic side, and wet seal area of MCFC, and hence the ideal material for bipolar plate current collectors should have acceptable corrosion resistance for all of these atmospheres. Stainless steels like 310 S (24–26 wt. % Cr) and 304 L (16–18 wt. % Cr) have emerged as materials of choice for MCFC hardware [1]. However, the hot corrosion in the presence of the carbonate melt is a critical issue with these materials for long-term operation. During the period of initial operation, the mechanism of corrosion in these steels is normal corrosion involving scaling via the formation of a layer of iron oxides on the chromium-rich oxide layer. One of the methods of protecting and improving the corrosion properties of steels is the application of coatings based on nitrides. The corrosion resistance of Cr-N coatings is better than that of the stainless steel and other nitride coatings in the high temperature pressurized water and the oxidation rate in air at 600/800°C is low [2].

304L stainless steel specimens of sizes 0.4 × 25 × 25 mm^3 were used as substrates. The coatings were deposited on polished stainless steel samples using a Cr cathode and the vacuum arc method. The chamber was evacuated to a pressure of 1×10^{-3} Pa. Argon gas was introduced into the vacuum chamber up to pressure 5×10^{-2} Pa for stable burning of the arc discharge. During the deposition of the chromium nitride layer, the nitrogen filling pressure was 2 Pa (variant #1 and #3) and 0.2 Pa (variant #2 and #4 Table 1). To avoid diffusion of chromium from the substrate during long-term oxidation, it was suggested to apply a protective copper sublayer (variant #3 and #4 Table 1).

Table 1. PVD modes and thickness of the obtained coatings

	Pressure of N_2, Pa	Bias voltage, V	Thickness Cu, µm	Thickness CrN, µm
#1	2	150	-	16.6
#2	0.2	120	-	6.9
#3	2	150	0.3	4.1
#4	0.2	120	0.3	2.2

The X-ray diffraction study was performed in monochromatic Cu Kα radiation using STOE powder diffraction system in a focusing Bragg-Brentano geometry (Fig. 1). Oxidation resistance and electrical conductivity of coatings after long-term (1000 h) holding at 600°C in air were studied. Electrical conductivity of obtained coating was $3.5\cdot10^5$ S/m.

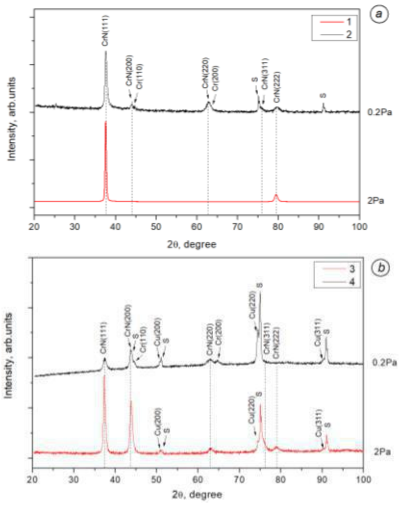

Figure 1. X-ray of samples with coatings of the Cr-N system deposited on a steel substrate without Cu sublayer (*a*) and with Cu sublayer (*b*).

It was established that coating variant #1 has the highest oxidation resistance, but coating variant #4 has greater electrical conductivity after long-term exposure at 600C in air.

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CATALYST & ACTIVE MATERIAL SYNTHESIS

Investigations of activated carbon from different natural sources for preparation of binder-free Few-walled CNTs/activated carbon electrodes

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Energy storage has become one of the main drivers of technological progress, as industrial and transportation activities are now heavily reliant on the combustion of fossil fuels [1]. The search for environmentally friendly, commercially available, and energy efficient systems is the objective of numerous research efforts. Batteries, fuel cells, and electrochemical capacitors (ECs) are the most common electrical energy storage devices, each working on different principles [2]. The main principle of batteries and fuel cells is based on converting electrical energy into chemical energy through redox reactions in the anode and cathode materials [3]. ECs are power devices that can be fully charged or discharged in seconds, also known as supercapacitors, ultracapacitors, or "double layer capacitors". Electric energy is stored through ion adsorption or fast redox reactions on the surface of the active material, which has an unlimited service life in charge/discharge cycles [4,5].

The active material is used in powdered form to create a porous structure with a high specific surface area that is available for electrochemical reactions. Polymer materials are added to the active material to form a usable electrode. Due to the insulating nature of the polymer materials, various forms of conductive carbon materials are added to increase the conductivity of the electrode. The mass fraction of the polymer binder is 10 20 wt.%, and the conductive additive is 5 15 wt.% of the total electrode mass. However, even with the addition of conductive agents, the electrode efficiency is still relatively low (usually about 1 ohm/cm or less). The low conductivity of the electrode necessitates the use of a metal with high conductivity, called a current collector. During charging, electrons quickly spread throughout the two dimensional surface of the electrode to the current collector, and they only need to pass through the thickness of the electrode to reach all of the active material. The current collector also functions as a substrate and mechanical support for the electrode material. Although some electrode compositions can form a separate film or sheet, the substrate usually plays a crucial role in maintaining the structural integrity of the electrode throughout the production and service life of the device. Traditionally, the electrode consists of 80% active material by mass, while the other 20 wt.% is made up of inactive elements (binder and conductive additive). Therefore, to increase the specific energy of batteries and electrochemical capacitors, it is important not only to use active materials that can store more energy but also to minimize the inactive weight required to create the final device.

This study presents the results of producing activated carbons (AC) through thermal treatment of plant based raw materials of various origins, including rice husk, apricot stones, walnut shells, beet pulp, and sunflower seeds, which were used to manufacture composite electrodes. The investigation of different sources of AC enabled the selection of the best raw material. The carbonization and thermal decomposition behavior of the raw materials were investigated using differential scanning calorimetry, while the AC samples were characterized using nitrogen adsorption, BET analysis, SEM, EDAX analysis, TEM, and Raman spectroscopy. A methodology for obtaining a flexible, ultra light hybrid electrode with high specific capacitance based on AC and carbon nanotubes (CNTs) is also proposed. The AC electrodes showed a high specific capacitance of approximately 172 and 119 F/g at scan rates of 5 and 100 mV/s, respectively. The use of domestically produced AC with a surface area of 2000 3000 m2/g resulted in electrode materials with higher specific capacitance compared to electrodes produced using traditional methods. The AC/CNT electrodes also exhibited low resistance. These findings demonstrate the potential of AC electrodes as a promising alternative for use in high performance energy storage devices. In the authors' opinion, this study highlights the importance of investigating different sources of raw materials, such as rice husk, apricot stones, walnut shells, sugar beet pulp, and sunflower seeds, to identify the most suitable precursor for the production of high performance AC electrodes.

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Cathode Active Material Synthesis and Battery Performance Tests for Li-ion Batteries from Domestic Raw Materials

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The energy requiremenet brought by technological developments from the past to the present evolves depending on the society's desire to be mobile, which is increasing day by day. Many technological devices such as electrical vehicles, smart phones, computers, drones, cameras meet the required energy from rechargeable lithium-ion batteries. However, the increasing world population and the increasing specifications of the technological devices developed in parallel with the per capita energy consumption by making the raw material resources needed for the production of these technological devices even more important. Nickel, cobalt and manganese compounds, which are the main raw materials used in the cathode production of NMC type lithium-ion batteries, are among these chemicals of strategic and critical importance, and the production of these chemicals in appropriate quality is of great importance for the industrial development of lithium-ion-based domestic battery technologies in our country.

Meta Nikel Kobalt A.Ş., which is the first and the only nickel-cobalt plant in our country at industrial scale. In Gördes plant, nickel-cobalt-manganese hydroxide intermediate product concentrate (MHP) is produced from Gördes lateritic ore using high-pressure acid leaching technology and is currently completely exported to overseas. However, due to the responsibility of transforming domestic resources to high value-added technological products and obtaining value-added products, research in this field has been regarded and the necessary technological infrastructure and specific knowledge have been created.

Within the scope of this study, precious metals in the MHP intermediate product obtained from Gördes lateritic ore were leached and valuable elements are taken to the liquid phase and crystallized after further purification processes such as solvent extraction and ion exchange. As a result, metal salts with purity up to 99.99% were obtained. The obtained nickel, cobalt and manganese sulphate salts were precipitated together with the developed co-precipitation process to obtain precursor in the form of NMC 622. After that, the precursor is treated with lithium and the cathode active material (CAM) is obtained by going through various heat treatments.

Figure 1. MHP product and produced sulfate salts (nickel, cobalt and manganese sulphate respectively) and CAM

The coin cell made with the CAM obtained from domestic raw materials showed a capacity of 184.55 mAh/g at 0.1C. It showed a capacity of 170.58 mAh/g in the first cycle and 157.45 mAh/g in the 50th cycle at 0.5 C, and the capacity conservation was calculated as 92.3% after 50 cycles at 0.5 C. The CAM obtained in the pilot-scale studies carried out according to the lab-scale developed process andsent to TUBITAK RUTE to make pouch type battery.

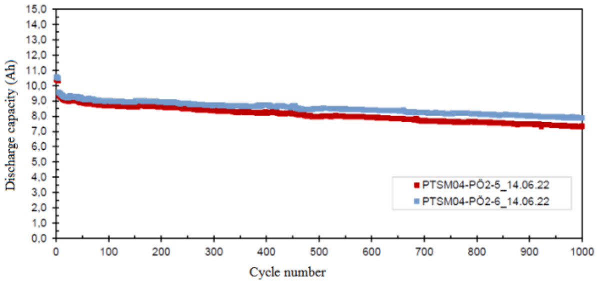

Figure 2. Pouch type battery cycle number and discharge capacity graph

In the 10 Ah capacity cells of the produces pouch type, 82% capacity conversation has been achieved as a result of 1000 cycles at a charge/discharge rate of 0.5 C at 100% CoC(Dept of Discharge) in the voltage range of 3-4.15V.

Acknowledgements

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ChCl:EG based solvometallurgical extraction of cathode active powder from spent lithium-ion batteries

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The recovery of lithium-ion batteries is essential to reduce potential environmental problems due to their toxic components which are critical primary sources. To reduce greenhouse gas emissions and transition to low-carbon extraction of critical metals, usage of solvometallurgical methods have increased in recent years.

The solvometallurgical leaching is a “green chemistry” application which uses the solvents based on renewable resources, biodegradable and reducing the environmental impact of the recovery process. Solvometallurgy becomes a prominent method owing to the minimum use of water, lower temperatures, almost no processing wastes and using of non-toxic solvents compared to the classical leaching methods. Additionally, solvometallurgical methods can be used to recover a wider range of metals from a variety of sources [1,2].

In this study, spent lithium-ion battery cathode active powder from same brand and same model (Bower-Original) was used as a raw material which includes Li, Ni, Mn, Co metals. Spent lithium-ion batteries were discharged in acetic acid solution for 24 hours to prevent short circut problems during dismantled of batteries. Cathode active powder were striped from cathode plate manually from aluminium foil to increase leach efficiency due to reduced amount of redundant components. XRD, TG/DTA, SEM and ICP-MS analyses were performed to characterize the cathode active powder. Based on XRD analyses, the peak observed for $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ is characteristic of NMC cathode material and can be fitted within the 96-400-2444 ICDD number. In addition to the $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ peak, a $LiMn_2O_3$ peak can also be observed in the 96-210-7267 ICDD number.

Figure 1. Oil-heated borosilicate reactor.

ChCl:EG (Choline Chloride:Ethylene Glycol) was selected as leaching solvent. Leaching processes were carried out in oil-heated, borosilicate glass reactor with 100 mL capacity (Figure 2). Leaching temperature selected between 80^{o}C-160^{o}C for ChCl:EG experiments. The solid/liquid ratio and stirring speed used in the process were both kept constant at 1:100 and 375 rpm, respectively. Leaching time (4-12 h) and temperature effects to leaching efficiencies were investigated. The leaching efficiency of the metals were determined by ICP-MS analysis of the leach solution.

The results of the analysis indicate that increasing the process temperature and reaction time had a positive impact on the leaching behavior of the cathode materials. This can be attributed to the fact that higher temperatures and longer reaction times promote greater solubility and reactivity of the cathode materials in the solvent system. The increase in temperature can enhance the rate of the reaction and facilitate the dissolution of metals from the cathode material into the solvent while longer reaction times provide sufficient contact time for the solvent to dissolve more of the target metals from the cathode material. Consequently, it can be inferred that optimizing the process temperature and reaction time can lead to improved leaching efficiency of the cathode materials, which can be advantageous for the recovery of critical metals from spent lithium-ion batteries.

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Nonosized $LiFePO_4$ manufacturing by ball-milling synthesis for Li-ion batteries

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Lithium iron phosphate ($LiFePO_4$) has emerged as a promising cathode material due to its attractive features such as high thermal stability, low toxicity, and extended cycle life. $LiFePO_4$ belongs to the olivine group of compounds and consists of a three-dimensional framework comprising iron-oxygen octahedral linked by phosphate tetrahedral (pnma structure). Despite its lower theoretical capacity of 170 mAh/g compared to other cathode materials, $LiFePO_4$ has high rate capability and stability at elevated temperatures, making it an appealing candidate for rechargeable lithium-ion batteries.

The manufacturing process of $LiFePO_4$ is complex and involves several critical steps as raw material preparation, cathode material synthesis, electrode fabrication, and cell assembly. Control of the raw materials and production processes is crucial to ensure high-quality and consistent performance of the resulting battery cells.

The olivine-structural phosphates have been synthesized by different techniques to improve their electrochemical property, i.e. hydrothermal methods followed by several high-temperature methods [1]. However, the manufacturing cost of such materials/methods is still a hurdle in their utilization for large battery systems. The proposed methodology consists of two stages, namely, mechanical activation (MA) of solid precursors in planetary ball mill and heat treatment in inert atmosphere at a relatively low temperature in the range of 500
optimized by changing MA parameters and including solid diluent to the reaction system.

The ball milling method involved mixing the raw materials in specific stoichiometric ratios, followed by activation of the mixture in a high-energy ball mill (fig.1.)

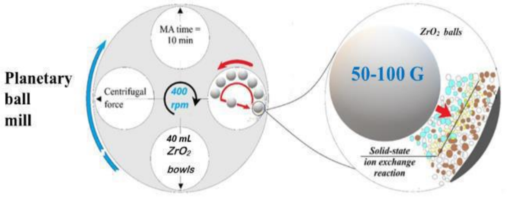

Figure 1. the operation of a planetary ball mill

The mixture of precursors $FeC_2O_4 + Li_2CO_3 + NH_4H_2PO_4$ were used to prepare $LiFePO_4$/C cathode material [2]. The resulting powder has been annealed at high temperatures in an inert atmosphere, such as argon, helps to eliminate any impurities and improve the crystallinity of the material, which can enhance its electrochemical properties.

After mechanical activation and heat treatment in the presence of sucrose as carbon source, nanoparticles were obtained. The electrochemical properties of the half-cell cell, where $LiFePO_4$ nanoparticles are used as a cathode, results show stable performance for 30 cycles with 100% coulombic efficiency.

For the scaling up of LFP manufacturing the ball milling is a promising method due to its ease of implementation, and scalability.

The detailed electrochemical performance and characterization of solidstate synthesized $LFePO_4$ nanoparticles-based cathodes will be presented.

Acknowledgements

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Phosphate cathode materials for lithium-ion batteries: on the way from $LiFePO_4$ to $LiMnPO_4$

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Phosphate cathode materials are a major alternative to oxide compounds as lithium ion battery (LIB) cathodes, primarily due to the success story of lithium iron phosphate $LiFePO_4$, often referred to as LFP. The main difference between phosphate and oxide materials is the presence of phosphate (PO_4) or pyrophosphate (P_2O_7) groups, which form a reliable structural framework and "bind" oxygen anions. Due to these factors, phosphate based materials show stable cycling over thousands of charge discharge cycles, the ability to charge or discharge quickly, and increased thermal stability, i.e. safety of use. At present, LFP has become the basis of a whole area both in research activities and in the field of the LIB industry an actively developing and extremely promising.

In the course of our work, we have studied many options for the synthesis of LFP, with an emphasis on the solvothermal synthesis method. The report will discuss the features of the structure of phosphate materials and the effect of various defects on their electrochemical properties, the relationship between synthesis methods, the morphology of materials and their characteristics, as well as the prospects for alternative LFP compositions to further improve the performance of LIB batteries. As an example, so colled Li rich olivines obtained by means of solvothermal method will be discussed.

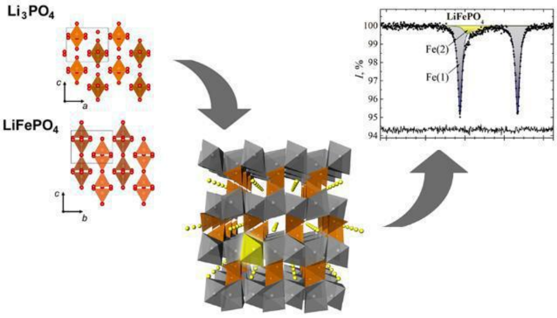

Figure 1. Li rich olivines: origin of formation and MS spectra "signature".

We observed that presence of a certain amount of Li^+ in M2 position in the crystal structure of the initial phosphate leads to appearing of additional component in Mössbauer spectroscopy (MS) spectra of all studied compounds, corresponding to ferric ions in the same position with distorted second coordination sphere. Evolution of MS spectra during charge/discharge revealed clear connection between relative contribution of this component and the mechanism of Li^+ (de)intercalation. Extended single phase regions with large Li^+ non stoichiometry in triphilite and heterosite phases of $Li_{1\ x}FePO_4$ observed by means of synchrotron X ray powder diffraction (SXPD) appear due to Li Fe defects existing in Li rich olivines and acting as a "diluting" agent preventing two phase spinodal decomposition. These features can be regarded as an additional merit of Li rich olivines [1] as a promising cathodes for high power Li ion batteries.

In addition, the main difficulties that arise when trying to increase the energy intensity of cathode materials by completely or partially replacing iron with manganese, as well as possible ways to overcome them, will be considered.

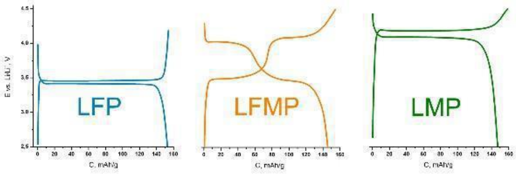

Figure 2. Charge discharge curves of the $LiFePO_4$ (LFP), $LiFe_{0.5}Mn_{0.5}PO_4$ (LFMP) and $LiMnPO_4$ (LMP) cathode materials.

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Optimization of electrochemical performance of NMC cathode via adjacent synthesis and test protocols

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$LiNi_xMn_yCo_{1-x-y}O_2$ (so-called NMC) has demonstrated the most effective combination of nickel, manganese, and cobalt for the cathode materials to yield better performance in terms of specific energy and power density, life span, costs and safety at Li-ion Batteries-LiB [1]. Nickel is responsible for high energy density and good storage capacity of LiBs, but suffers from low thermal stability and insufficient cycle life [2]. Considering these deficiencies, the NMC compositions are designed to include Manganese which acts not only as a stabilizer, but also prevents Nickel oxidation and thus, reduces the risk of capacity fading. Moreover, a new generation of cathode microparticles have been emerged aiming in a clever integration of Manganese in NMC morphologies by their core/shell structured designed synthesis. This special morphology provides surface stabilization of Ni-rich NMC by Manganese rich shell, to keep the energy storage capabilities at a higher level and thus, preventing the early cathode degradation. The strong dependence of the NMC cathode's functional properties on the relative ratios of the involved transition metals as well as the insufficient understanding of the synergistic effect of core and shell during the electrochemical tests, forced the researches to explore new synthesis approaches to enhance the overall performance of cathodes with this new structural design.

In this work, the cathode powders having Ni-rich Core/Mn-rich Shell have been synthesized via a cost efficient and easy controlled process that is built on a two-step co-precipitation method by optimization of process parameters under steady performance tests. These include variation of synthesis steps, co-precipitation agents, Li-infiltration approaches, heat treatment conditions as well as establishment of the proper synthesis protocols to fabricate NMC cathodes with a good electrochemical performance for Li-ion batteries. In order to identify the morphological, dimensional, structural and compositional relations within the core/shell particles SEM, EDX and XRD techniques have been employed. It has been shown that thermal treatment (temperature, duration, heating rate) slightly effect the morphology of the obtained particles, however relying on to the generated XRD analysis, plays a significant role in the achievement of the best NMC crystalline phase composition by avoiding undesirable for batter performance compounds. In turn, it is observed that a likely non-efficient Li-infiltration results in poor electrochemical performances. Electrochemical characterization by means of EIS spectroscopy and CV tests indicated that the combination of crystalline phase composition, the presence of the residual Li-based compounds, as well as Li incorporation approach has a high impact on the electrochemical properties of the obtained core/shell structured NMC cathode powder.

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One-pot synthesis of free-standing $LiCoPO_4$/C composite nanofibers as high-voltage cathode materials for lithium-ion batteries

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Introduction

Lithium cobalt phosphate (LCP) is a high-voltage lithium-ion cathode material which appears to be appealing due to its high theoretical capacity of 170 mAh g^{-1} with higher energy density compared to lithium iron phosphate, as its redox potential is 4.8 V (vs. Li/Li^+) [1]. The main challenge limiting the practical capacity and cyclability of LCP is its low electrical conductivity.

In this work, we propose one-pot synthesis of LCP nanoparticles incorparated within carbon fiber matrix by electrospinning with heat treatment to improve the electrical conductivity of the cathode material. Pre-oxidation temperature of the precursor fibers was varied to find the optimal carbon content for the best electrochemical performance.

Experimental details

Electrospinning solution was prepared as reported elsewhere [2] with the addition of stoichiometric amount of lithium nitrate and electrospun under voltage of 18 kV, tip-to-collector distance of 10 cm, flow rate of 1 mL h^{-1}, making use of a drum-type collector. Fibers were dried at 150 ºC, pre-oxidized at different temperatures, and heat-treated at 700 ºC in N_2 atmosphere. The crystal structure and the morphology of nanofibers were studied by X-Ray diffraction (XRD, Miniflex, Rigaku) and scanning electron microscopy (SEM, Crossbeam500, Zeiss), respectively. The carbon content was determined by CHNS analysis.

Results and Discussion

Figure 1a shows XRD patterns of samples annealed in N_2 at 700 ºC after pre-oxidation at different temperatures. Formation of orthorhombic $LiCoPO_4$ with Pnma(62) space group can be observed in all three samples with a small impurity peak at about 22º, which decreases with increasing the pre-oxidation temperature.

Figure 1b shows the SEM images of prepared samples**.** In this case, several differences have been observed, including particle formation. Fibers of sample prepared by pre-oxidation at 300 ºC are more decorated with nanoparticles, while surface of samples prepared by pre-oxidation at 330 ºC and 350 ºC is more smooth and uniform, suggesting encapsulation of LCP nanoparticles within the fiber matrix.

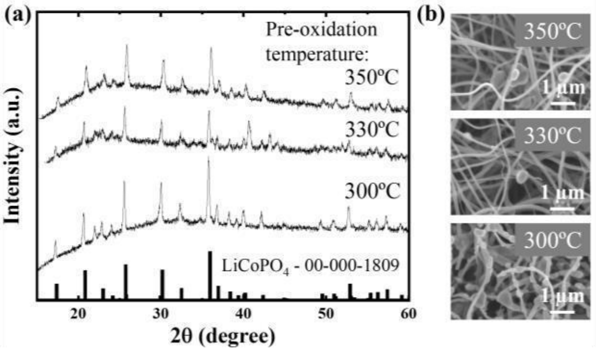

Figure 1. (a) XRD patterns and (b) SEM images of samples pre-oxidized at different temperatures.

The elemental composition of three samples determined by CHNS analysis is shown in **Table 1**. The difference in the pre-oxidation temperatures resulted in the differences in the carbon contents and C/N ratio of samples.

Table 1 Elemental composition determined by CHNS.

Sample	C, wt.%	N, wt.%	C/N ratio
300 ºC	17.0	2.8	6.0
330 ºC	16.7	2.9	5.7
350 ºC	11.5	2.3	5.1

Electrochemical properties of the obtained materials will be presented at the conference.

Acknowledgements

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The synthesis of carbon material from biomass for energy conversion and storage

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Energy has been one of the world's biggest concerns due to rising consumption and demand with the increase in population. The intensive use of fossil fuels to meet energy needs includes global warming due to CO_2 emissions and climate change due to global warming. The answer to halting climate change is renewable energy, and this strategy must be sustainable. The fact that intermittency of renewable energy sources such as wind and solar makes it necessary to design these systems in integration with energy storage systems.

One of the keys to the development of the next generation of biocompatible energy storage and conversion technologies lies in both finding new materials and understanding these materials' behaviors. Among the exploited energy materials, biomass-derived carbon, as a type of electrode catalyst materials, has attracted much attention due to its structural diversities, high electronic conductivity, adjustable physical/chemical properties, environmental friendliness, and significant economic value [1]. It has been reported that lignocellulosic biomass obtained from agricultural and forest residues is a suitable source for conversion into carbon materials [2]. Lignocellulosic biomass is rich in carbon and other important additives and, as a result, can contribute to the development of sustainable processes. In this study, hawthorn *(Crataegus Orientalis)* cores, which are agricultural waste, were used as raw materials to produce activated carbon.

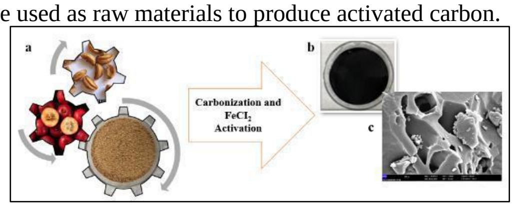

Figure 1. a) ground hawthorn cores b) activated carbon c) FE-SEM image of activated carbon

Firstly, hawthorn cores were carbonized by pyrolysis in an inert condition, resulting in a solid residue with increased carbon content. Prior to activation, biochar was impregnated with $FeCl_2$/ethanol solution in a 1:10 mass ratio ($FeCl_2$:Biochar). After 30 minutes of impregnation, filtrated, and then the mixture was dried in a vacuum drying oven at 80 °C to ensure complete drying. Finally, it was kept under N_2 flow for 1 hour with a temperature increase of 800 °C and 5 °C/min, and the active carbon obtained as called HS-AC.

The synthesis diagram of HS-AC was exhibited in Figure 1. The morphology of HS-AC was characterized via a Field Emission Scanning Electron Microscopy (FE-SEM) and the images obtained from this analysis was given in Figure 2. As is seen from this figure, HS-AC showed a well-developed porous structure. The activation process resulted in the formation of pores and the significant removal of inorganic material. Also according to the FE-SEM EDX analysis, the composition of the elements in HS-AC was as follows: 95% for carbon, 0.26% for oxygen, 1.35% for chloride, and 0.41% for iron.

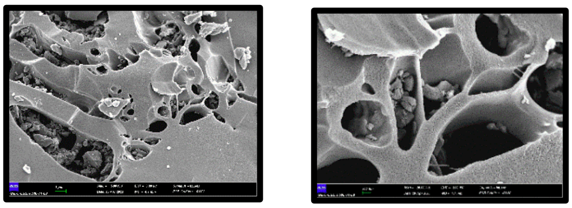

Figure 2. FE-SEM images of HS-AC

It can be concluded that $FeCl_2$ is a promising activating agent to prepare activated carbon with a developed porous structure. Consequently, HS-AC can be considered as carbon material with low-cost and eco-friendly. Furthermore, this material can be use as efficient electrocatalyst for energy storage and conversion technologies.

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Some aspects of the synthesis and application of nanomaterials

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This paper presents the results of some investigations into the production of various nanoscale materials that have been carried out at the Institute of Combustion Problems in recent years.

1.Synthesis of hydroxyapatite and potential biomedical applications.

Although bone fractures are a major public health concern worldwide, their incidence and costs have not been thoroughly investigated. Fractures are the main issue with bone illness, especially osteoporosis, and may be the patient's first obvious symptom. For example, an estimated 2 million people in the US annually experience a fracture. It was discovered that the crystalline HA powder obtained from an aqueous solution through chemical precipitation using a biological eggshell waste has a purity of ~95%. According to EDX analysis, the Ca/P ratio is 1.5, which is suitable for medical uses and improves the osteogenesis properties of scaffolds. The experimental data confirm that obtained polymer-based fibers by electrospinning with the addition of HA particles are well-qualified candidates for use as biological matrixes and drug delivery agents in TE and can reduce the convalescence period. According to the results, among the TPMS structures, the Gyroid structure is the best in Top-load/Crush test, and the Lidinoid structure is the best in Tensile tests. However, it was found that adding the resin reinforce precursors to the matrix positively affects the mechanical properties, enhancing osteogenesis and reducing the convalescence period. In addition, obtained data from actual mechanical tests agree with the simulation data and confirm the method. Producing resin reinforce precursors by ultrasonic method led to the formation of nanomaterials with suitable size, morphology, and surface properties for medical applications.

2.Obtaining nanostructured fibers modified by nickel oxide particles and their use in chemoresistive sensors.

Electrospinning is a widely used process for producing fibres with diameters ranging from nanometres to micrometres. One critical factor in electrospinning is the choice of polymer, which can affect the morphology, structure and properties of the resulting fibres. While polyacrylonitrile (PAN) is a popular polymer for electrospinning, coal tar pitch (CTP) has attracted attention as an alternative due to its unique properties. The use of CTP instead of PAN in electrospinning has great potential to produce fibers with improved properties. The obtained fibres have been modified by nickel oxide nanoparticles. As a result, the nanostructured fibres can be effectively used as gas-sensitive materials. Carbon/NiO fibers with a diameter of 100-300 nm were obtained. It was established that sensitivity to acetone equal to 73% is achieved by doping carbon fibres with nickel oxide nanoparticles of average size 48 nm, thereby increasing the surface area for gas adsorption and detectable gas reacts chemically with nickel oxide nanoparticles, resulting in changes in the electrical conductivity of fibres.

3.Synthesis of composite pyrotechnical materials and optimization of effective conditions for their practical application in the destruction of rock formations.

The effect of different types of carbon powders on the combustion of gasifying compositions based on sodium nitrate and magnesium were investigated. A preliminary thermodynamic analysis of gasification processes of multi-component compositions was carried out using the TERRA software package for modelling phase and chemical equilibria. The methodological basis of the calculation included an evaluation of the fundamental laws of thermodynamics together with the laws of conservation of mass, energy and charge. The TERRA software is linked to a database of properties of individual substances (about 3500 substances in gaseous, ionised and condensed states), which allows simultaneous consideration of systems containing up to 25 chemical elements. The condensed compounds and gas phase components to be considered in the calculations are automatically selected from the database. Up to 200 condensed compounds and up to 500 gaseous substances can be calculated as possible components of a given equilibrium state. In order to find the optimum ratio between oxidant ($NaNO_3$) and fuel (Mg + C), systematic calculations of the thermodynamic equilibrium properties were performed by varying the mixture composition. Experimental measurements of the combustion rate, flame temperature and composition of the combustion products for two types of carbon were carried out to better evaluate the characteristics of the investigated mixtures. The measurements were carried out in air to obtain preliminary information on the feasibility of layer-by-layer combustion for the selected compositions. Also it is planned to carry out similar measurements at higher pressures.

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Nitrogen-Doped Electrocatalyst from Tangerine Peels-Derived Biochar for Energy Storage and Conversion Applications

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Investigating effective and fairly cost electrodes with considerable energy efficiency and power density is important for electrochemical energy storage and conversion devices. Today, carbon-based materials such as activated carbon, graphene, and porous carbon, especially synthesized from wastes, stand out as electrode materials in energy storage and conversion applications due to their wide usability, economic applicability, high surfaces, and pore sizes.

Citrus fruits are one of the biocarbon material groups. Tangerine, which is a citrus fruit, is one of the most grown and consumed fruits in Turkey. Detailed production and consumption data for tangerines in Turkey can be found in Table 1 [1].

Table 1. Tangerine production/consumption data in Turkey

Year	Production (Tonne)	Consumption (Tonne)
2021/22	1.819,000	854.807
2020/21	1.585,629	699.033
2019/20	1.400,000	594.829

In this study, it was aimed to obtain activated porous carbon from tangerine peels. The peels of tangerines grown in Adana were used. Based on elemental analysis, the tangerine peel obtained from Adana was found to contain 45.8% carbon. As firstly, the tangerine peels were ground and pyrolyzed. Then, nitrogen-doped carbon electrocatalysts were synthesized from the tangerine peel powder by using NH_4OH via the hydrothermal carbonization (HTC) method. The products of different steps in this method were shown in Figure 1.

Figure 1. Synthesis of porous carbon from tangerine peels

The morphologies of the obtained activated porous carbon samples were analyzed using Field Emission Scanning Electron Microscopy (FE-SEM EDX) and Raman spectroscopy. FE-SEM EDX analysis showed that the nitrogen-doped carbon sample consists of 81.99% carbon, 12.92% oxygen, and 5.1% nitrogen. The porous structure of the sample also can be seen in Figure 2. In Figure 2, the FE-SEM images of the samples produced by HTC method were given. As seen in the FE-SEM results, the synthesized carbon materials have a porous structure.

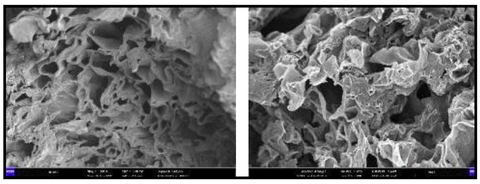

Figure 2. FE-SEM analysis of porous carbon from tangerine peels

As a result of the porous structure obtained, it is expected to obtain electrode applications with higher activity values to be used in energy conversion systems by increasing the active surface area of the material. According to the Raman analysis, the characteristic D and G bands of the obtained sample were seen at 1340 cm^{-1} and 1580 cm^{-1}, respectively, indicating the presence of carbon structures.

In conclusion, tangerine peel, which is a fruit waste with high waste potential, is an important biomass precursor to obtain nitrogen-doped carbon electrocatalysts with simple and cost-effectiveness. Moreover, the high electrochemical performance of the resulting carbon material renders it a suitable candidate for electrocatalysts in energy conversion and storage devices. In addition, this is an environmentally friendly alternative solution since as recycling tangerine production wastes can aid in mitigating environmental pollution.

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Atomic structures for ABO_3 perovskite

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Barium titanate - perovskite was discovered half a century ago, but due to its unique crystal structures, physical and chemical properties, the material still attracts a lot of attention of researchers. In addition, barium titanate has a high dielectric constant, and their excellent piezoelectric and ferroelectric properties are also known. Over the past decade, it has become one of the important materials with excellent dielectric, ferroelectric and piezoelectric properties, due to which this type of material has great capabilities, which allows them to be used in the production of electronic devices. It is one of the most thoroughly studied cubic perovskites, and has paraelectric properties at high temperatures and has a simple cubic perovskite structure. Most of the ABO_3 type perovskites have the same stable phases at different temperatures.

Perovskites can exist in various phase modifications, which generally exhibit different properties. The number of phase modifications depends on the specific combination of A and B cations [1, 2]. Many perovskites, specifically, demonstrate the presence of other phases. The highly symmetrical cubic phase of the *Pm-3m* crystal is also stable at high temperatures and demonstrates a series of three phase transitions with decreasing temperature: tetragonal *I4/mcm* at 393 K, orthorhombic *Amm2* at 278 K and rhombohedral *R3m* at 183 K, as shown in Figure 1.

Over the past 20 years, several first principles calculations have been carried out, in which more attention was paid to the structural and electronic properties of the four phases [3]. Perovskites are complex oxides, mainly of the composition ABO_3, where A is a divalent metal, and B is a tetravalent (transition) metal. DFT calculations are carried out with high accuracy to precisely obtain ferroelectric phases. Minimization is not required for a cubic structure. The tetragonal structure was optimized by changing the coordinates of the ions, since the symmetry (distortion in the z direction) allows optimization in a fixed c/a ratio, while maintaining a fixed volume. The theoretical study of this perovskite still requires detailed analysis, since it does not show the same result compared to experimental data and still remains an object research. Experimental data showed band gap widths of about 3.7 eV for the cubic phase and 3.9 eV for the tetragonal phase. In general, density functional theory (DFT) will be applied with a combination of different approximations to describe the structure of the perovskite band gap.

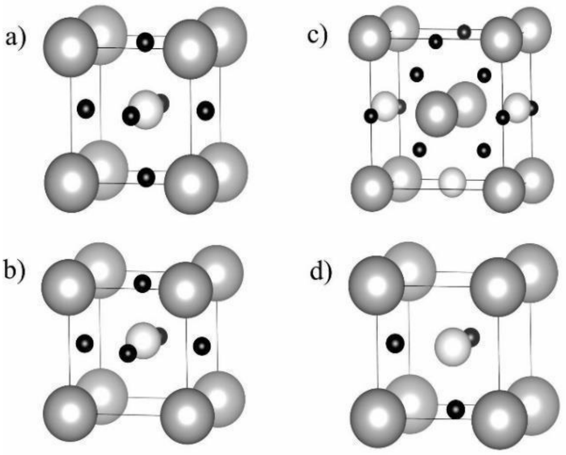

Figure 1. Unit cells $BaTiO_3$ in cubic, tetragonal, orthorhombic and rhombohedral phases.

Then, using the optimized coordinates of the ion particles, the relation (maybe the ratio) $^{c}/_{a}$ was optimized at a constant volume. Thus, the relation $Ti(1/2, 1/2, 1/2 + \Delta z_{Ti})$, $O_1(1/2, 1/2, \Delta z_{O_1})$, $O_2(1/2, 0, 1/2 + \Delta z_{O_2})$ it has been optimized while minimizing. The lattice parameters were also optimized in the orthorhombic phase: a, b, c and $Ti(1/2, 0, 1/2 + \Delta z_{Ti})$ $O1(0, 0, 1/2 + \Delta z_{O1}), O2(1/2, 1/4 + \Delta y_{O2,} 1/4 + \Delta z_{O2})$. Lattice parameter a $(a = b = c)$, angle α $(\alpha = \beta = \gamma)$ $\Delta\, Ti(1/2 + \Delta x, 1/2 + \Delta x_{Ti,} 1/2 + \Delta x_{Ti})$ $O(1/2 + \Delta x_O, 1/2 + \Delta x_{O,} 0 + \Delta z_O)$ were optimized values for the rhombohedral phase.

Acknowledgements

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Research of hybrid perovskite - low dimensional materials

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The discovery of semi-metallic graphene, which is a two-dimensional allotropic modification of carbon formed by a carbon layer one atom thick, created a powerful theoretical and experimental prerequisite for the development of two-dimensional film materials (2DLM). In other hand, two-dimensional transition metal oxide films (TMO) are currently important both in fundamental research and in technological applications due to their wide range of material properties from semiconductors, metals to superconductors. However, a material with fixed properties may not have universal application. Due to the unique crystal structures, physical and chemical properties, 2D TMO can be efficiently configured using various strategies such as size reduction, intercalation, heterostructure, doping and gating. The structures created by the combination of two or more atomically thin graphene-like provided by van der Waals interactions. Hence, such heterostructures are called van der Waals vdW heterostructures [1].

Heterostructures based on graphene and two-dimensional films of nanostructured ($BaTiO_3$), ferromagnetic ($La_{2/3}Sr_{1/3}MnO_3$, $SrRuO_3$), transition metal oxides are promising for the development of new multifunctional materials for memory cells, quantum computer elements, Li-battery anodes, (photo)catalysts, supercapacitors, transistors, sensor materials, solar panels, fuel cells, electrochromic devices. These materials change the properties of the initial structures, and a material with new hybrid properties appears, which opens up new paradigms for the development of new materials and nanodevices. Strong covalent bonds ensure the planar stability of 2D crystals, and the connection between different layers. In presented paper the heterostructures on the base of from perovskite and layered structure was simulated and considered electronic, optical and properties for energetical applications with ab-initio methods.

It was predicted that the creation and management of such d-states could be realized by introducing impurities into the TMO. In our work, the necessary TMO with unique properties created in this way will be an object for substantiating various physical and chemical properties.
Also, during the project implementation, it is important to determine, in accordance with the Mermin-Wagner theorem [14], whether a stable state of symmetry is maintained at a finite temperature in systems with sufficiently short-acting interactions at dimension $d \leq 2$. Consequently, short-acting fluctuations are less preferable from an energy point of view.

The proposed goals and methodology will allow us to advance in understanding the existing problems in the study of quantum (film) materials. In particular, this will allow us to study the mutual influence of spontaneous ordering in the TMO with a decrease in the sample dimension.

First of all, it should be noted that all calculations will be performed within the framework of density functional theory DFT, DFT+U in the VASP software package. The study uses an integrated approach that includes the search and preparation of nanoclusters of the systems under consideration, descriptions and characterization of the structure and size by additional computational methods, calculation of electronic properties, visualization of the results obtained, as well as comparison of computational and experimental data. However, the accuracy of DFT depends on the correct choice of the exchange-correlation functional.

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Electrospun PCL (Polycaprolactone) Nanofibers and Their Reinforced Composites: Preparation, Modification, Applications, and Perspectives

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In recent decades, nanofiber membranes have gained significant popularity due to their unique characteristics, such as large specific surface areas, excellent permeability, interconnected pores, and exceptional functionality. Electrospun composite nanofibers have found diverse applications in various fields, including tissue engineering, wound healing, photonics, filtration, composites, as well as supercapacitors, and batteries [1-3]. These electrospun composite nanofibers offer tremendous potential for advancing technology and addressing a wide range of challenges in different industries.

Therefore, our research focuses on PCL (Polycaprolactone) nanofibers and their reinforced composites.

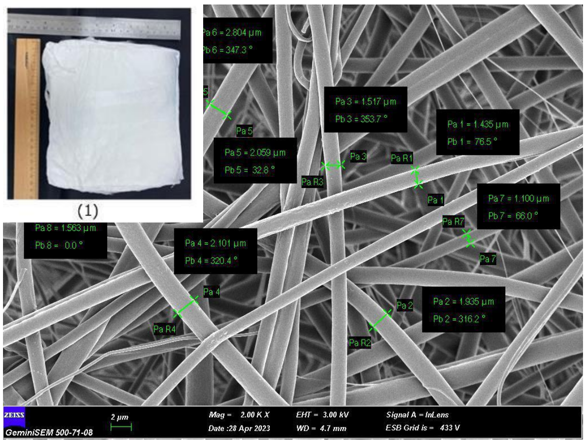

Figure 1. SEM image of PCL scaffolds.

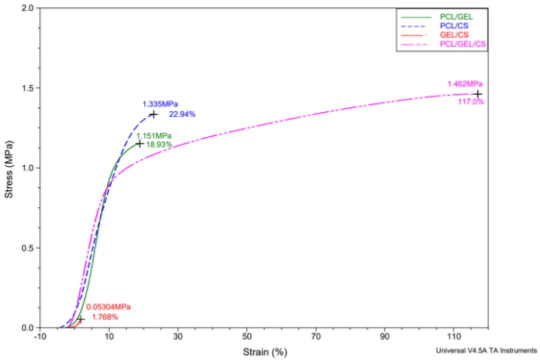

Figure 2. Stress-strain plot of nanofiber scaffolds

Acknowledgements

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Synthesis of materials with a hierarchical structure based on tin dioxide

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SnO_2-based hierarchical structures have been intensively studied because they have large surface area, high surface permeability, low density, low cost, environmental friendliness, and stable physicochemical characteristics [1]. This paper presents a way to create SnO_2-based hierarchical micro-nanostructures with controlled size. The proposed method is based on the use of the $SnCl_4$/EtOH/NH_4OH lyophilic film-forming system. Due to the greater stability of the properties of the films obtained from this film-forming system, with prolonged temperature exposure, the service life of the gas sensor is increased. Figure 1 shows the structure of films obtained from the $SnCl_4$/EtOH/NH_4OH film-forming system with different ratios of ammonium ions to tin ions by the sol-gel method. The photographs were taken with an MPE-11 optical microscope. Figure 1a shows that in the absence of ammonium hydroxide no regular structures are found on the film. When ammonium ions are added, certain structures begin to form, the shape and size of which depend on the relative amount of tin ions N(Sn) and ammonium ions N(NH_4). At N(Sn) > N(NH_4), structures resembling a six-petalled flower are formed (Figures 1b, 1c, 1d). The average size of the synthesized structures increases from 10 to 40 µm with an increase in the content of ammonium ions. At N(Sn) ≤ N(NH_4), the formation of cruciform structures predominates (Figures 1e, 1f). Their size is much larger than flower-like structures and reaches more than 300 µm. When the ratio of ammonium ions to tin ions is 2:1, structures with the largest size are formed.

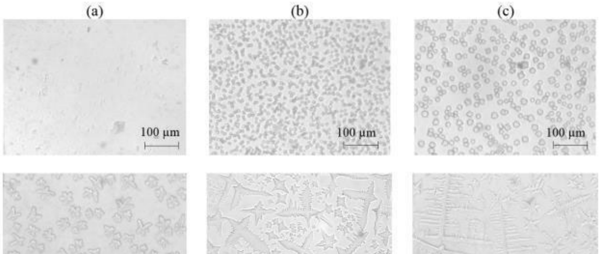

Figure 1 – The structure of the film obtained from the $SnCl_4$/EtOH/NH_4OH film-forming system by the sol-gel method, with different amounts of NH_4OH per 100 ml of solution: a) without adding NH_4OH; b) - 0.1 ml; c) - 0.2 ml; d) - 0.4 ml; e) - 0.8 ml; f) - 1.6 ml.

To study the crystal structure of the obtained films, measurements were made on a DRON-6 X-ray diffractometer. The measurement results are shown in Figure 2, in which we have marked the signal from the crystallographic plane NH_4Cl(110) and from the three crystallographic planes SnO_2(110), SnO_2(101) and SnO_2(211).

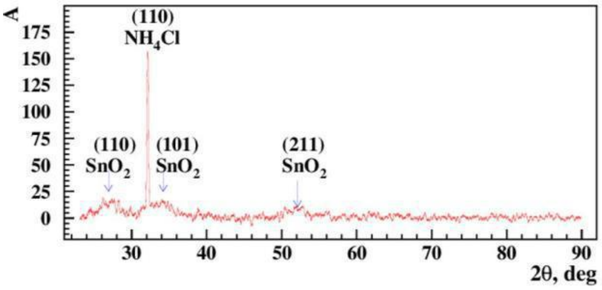

Figure 2 – X-ray diffraction pattern of the crystal structure of the film obtained from the $SnCl_4$/EtOH/NH_4OH film-forming system (with 0.8 ml of NH_4OH per 100 ml of solution) by the sol-gel method, measured on a DRON-6 X-ray diffractometer.

The average sizes of crystallites were calculated using the Scherrer formula, which relates the sizes of crystallites to the width of diffraction peaks [2]. The size of SnO_2 crystallites is 3.6 nm, and the size of NH_4Cl crystallites is 109 nm. Thus, SnO_2 and NH_4Cl are involved in the formation of the synthesized hierarchical structures.

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Effect of NH_4F additive on the electrical properties of nanosized tin dioxide films obtained from lyophilic and lyophobic film-forming systems

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Composite systems based on tin dioxide have many applications as a functional material [1, 2]. In this case, the properties of the resulting film can significantly depend on the method of obtaining a thin film. In this work, we studied the effect of NH_4F addition on the electrical properties of nanosized tin dioxide films obtained from lyophilic and lyophobic film-forming systems. Thin films of tin dioxide were obtained from 5 film-forming systems, including those containing NH_4F and NH_4OH dopants: $SnCl_4$/EtOH, $SnCl_4$/EtOH/NH_4F, $SnCl_4$/EtOH/NH_4OH, SnO_2/EtOH, SnO_2/EtOH/NH_4F. For a assessment of the contribution of doping additives to the conductivity of the films, calculations of the surface resistance, resistivity, and conductivity of the films under study were made. The results are presented in Table 1.

Table 1 – Surface resistance, resistivity, specific conductivity of the studied films

The composition of the film-forming system	R_{sh}, kOm/ square	ρ, Om*cm	1/ρ, $Om^{-1}*cm^{-1}$
$SnCl_4$/EtOH	15,6±1,4	0,390±0,035	2,6±0,2
$SnCl_4$/EtOH/NH_4F	6,7±0,6	0,097±0,008	10,3±0,8
$SnCl_4$/EtOH/NH_4OH	15,4±1,6	0,255±0,026	3,9±0,4
SnO_2/EtOH	78,9±6,9	0,512±0,044	1,9±0,2
SnO_2/EtOH/NH_4F	69,4±8,3	0,590±0,070	1,7±0,2

Table 1 shows that the addition of NH_4F to the lyophobic film-forming system SnO_2/EtOH did not lead to an increase in the specific conductivity. At the same time, the addition of NH_4F to the lyophilic film-forming system $SnCl_4$/EtOH leads to an increase in the specific conductivity by several times. This confirms the presence of fluorine ions as additional sources of free charge carriers in the composition of the films [3]. The addition of an aqueous ammonia solution to the $SnCl_4$/EtOH/NH_4OH film-forming system also led to an increase in the specific conductivity. Apparently, due to an unshared electron pair in the nitrogen atom.

X-ray diffraction analysis confirmed the presence of fluorine ions in the films obtained from the $SnCl_4$/EtOH/NH_4F film-forming systems. The X-ray diffraction pattern are shown in Figure 1. It can be seen that all films consist of SnO_2 crystallites. On the X-ray diffraction pattern of the film obtained from the $SnCl_4$/EtOH/NH_4F film-forming system, $SnOF_2$ peaks are observed. These peaks indicates the successful incorporation of tin ions into the film structure.

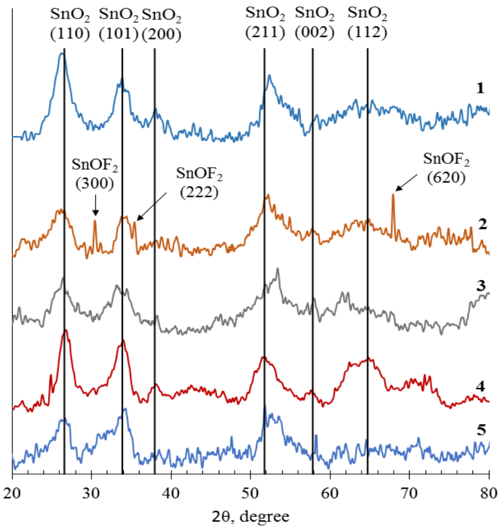

Figure 1 – X-ray patterns of thin films of tin dioxide obtained from different film-forming systems: 1 - $SnCl_4$/EtOH, 2 - $SnCl_4$/EtOH/NH_4F, 3 - $SnCl_4$/EtOH/NH_4OH, 4 - SnO_2/EtOH, 5 - SnO_2/EtOH/NH_4F

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Coal tar pitches / PAN based electrospun fibers

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The investigation work focuses on the obtaining of nanostructured fibers using polyacrylonitrile and technogenic waste, specifically coal tar produced from fossil coal coking. The resulting fibers are further modified with functional additives, including nickel oxide nanoparticles, nanoporous coals, and silicon dioxide nanoparticles. The physical and chemical properties of the modified fibers are experimentally investigated to evaluate their potential use as gas-sensitive and sorption materials.

Electrospinning is a well-established technique for producing fibers ranging in diameter from nanometers to micrometers. The process involves applying an electric field to a polymer solution or melt, resulting in a charged jet that is deposited onto a collector. The choice of polymer is a crucial factor in electrospinning as it can affect the morphology, structure, and properties of the resulting fibers. While polyacrylonitrile (PAN) is the most commonly used polymer for electrospinning, coal tar pitch (CTP) has emerged as a promising alternative due to its unique properties.

Coal tar pitch is a byproduct of the coal carbonization process and contains high molecular weight polycyclic aromatic hydrocarbons. CTP has a complex chemical structure and high carbon content, making it a suitable material for producing carbon fibers with high mechanical strength and electrical conductivity. Moreover, CTP is a low-cost and readily available material in our region. Usually, CTP is disposed of by incineration or landfill, which leads to environmental pollution. However, by recycling CTP to produce valuable carbon materials like carbon fibers, we can reduce the burden on the environment. In summary, electrospinning is an established technique for producing fibers, and CTP has emerged as a promising alternative to PAN due to its unique properties. By using CTP to produce carbon fibers, we can not only obtain materials with desirable mechanical and electrical properties but also recycle a waste product, reducing the environmental impact.

The use of CTP as an alternative to PAN in electrospinning is crucial for producing fibers with improved properties such as higher thermal stability, mechanical strength, electrical conductivity, and chemical resistance. With further research and development, CTP-based fibers have the potential to revolutionize materials science and significantly impact various industries. However, CTP presents some challenges in electrospinning, such as its high viscosity, which can affect the formation of a stable jet, and the requirement for high processing temperatures. Nevertheless, this paper presents optimized electrospinning parameters for CTP, which can serve as prerequisites for the production of fibers with controlled morphology and properties. For instance, we prepared a solution by combining PAN and CTP to reduce viscosity and enhance solution moldability. PAN is a widely used electrospinning polymer with low viscosity, making it a suitable additive for CTP-based fibers.

Based on our experimental work, we have established that the optimal weight ratio of PAN to CTP for producing carbon fibers is 70:30. Using this ratio, we were able to produce one-dimensional fibers with an average diameter of 248 nm and a carbon content of at least 92% through a one-stage electrospinning process. Carbon fibers doped with nickel oxide nanoparticles, with an average crystallite size of 48 nm obtained through solution-combustion synthesis, demonstrated a sensitivity of 73% towards acetone. The gas sensitivity analysis of the material yielded positive results, indicating excellent chemical stability and high sensitivity of the sample towards gaseous acetone.

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SYSTEM AND APPLICATIONS

TiO_2 nanotube-based solar cell combined with electrochemical capacitor

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Titanium dioxide (TiO_2) is a wide band gap semiconductor with a bandgap ranging from 3.0 to 3.2 eV, capable of converting light energy into chemical redox energy, making it an ideal material for harvesting solar energy and maximizing conversion efficiency in various applications, such as photovoltaics, microwave sensing, and photocatalysis. TiO2 assisted photoelectrolysis of water is achieved using a closed circuit photoelectrochemical solar cell consisting of a TiO2 anode and a Pt counter electrode exposed to near UV light. Typically, the anatase phase of TiO_2 is the most efficient for solar cell performance. Similarly, nanoporous anodic alumina (NPAAO) is an electrically insulating, optically transparent, and chemically stable material with widespread use in electronic, optoelectronic, and sensing devices, as well as a template for the synthesis of metallic and semiconductor nanowires. Both NPAAO and free standing vertically oriented nanotube TiO2 (TNT) can be fabricated via anodization and heat treatment of thin Al and Ti layers deposited on different substrates, such as Si or conductive glass substrates (InSnO or ITO covered), using electron beam evaporation or magnetron deposition. The electrochemical anodic oxidation process can be carried out in an electrochemical cell with a two or three electrode system, using a Ti or Al thin layer as the working electrode (the anode), Pt as the counter electrode, and a standard voltage source or a high voltage potentiostat.

Due to the intermittent and variable nature of solar energy intensity, which varies greatly depending on the season and time of day, combining solar cells with energy storage devices, such as Li ion batteries and supercapacitors (SC), in a single power unit component is essential [1,2]. In this study, we have utilized both AAO templates and TNT thin layers [2,3] to propose a device that integrates energy conversion (TNT based solar cell) and energy storage (SC based on NiO nanotubes synthesized in AAO nanopores) into a single system. The solar cell and capacitor are fabricated on opposite sides of a common glass slide wafer, both of which are covered with a conductive ITO layer. The TNT based solar cell is positioned on the front side of the device to receive light, while the SC is located on the rear side. Alternatively, a dye-sensitized solar cell or Grätzel cell [4] can be used as the solar cell component in the proposed hybrid device.

The supercapacitor component consists of freestanding NiO2 nanotubes that are electrochemically grown inside AAO nanopores and embedded in the electrolyte. They are electrically connected to the positive electrode through the ITO layer, while activated carbon serves as the negative electrode. The ITO layer acts as both the rear electrode for the solar cell and the positive electrode for the SC.

To realize the proposed device structure of AAO(NiO) /ITO/Glass/ITO/TiO2, we employed RF magnetron sputtering to obtain highly ordered TNT and AAO arrays with a high degree of optical transmission. Subsequent anodic oxidation and thermal annealing were also applied. Additionally, we developed a technique for the electrochemical deposition of nickel nanotubes into AAO pores and doping of TNTs with various impurities (nitrogen and CdS), which enhanced their photosensitivity from the UV region to the visible spectra. The device design enabled the combining and simultaneous execution of similar fabrication operations. The films were characterized using scanning electron microscopy, XRD, Raman spectroscopy, UV vis spectrometry, and spectroscopic ellipsometry. The resulting structure, with an outer TiO2 layer having an extended nanotube surface and an electrically conductive ITO layer, exhibited strong absorption of solar radiation, making it well suited for solar energy harvesting applications. Thus, the proposed device is a fully integrated device with a monolithic structure, where the solar cell and energy storage segments share a common substrate in the form of a transparent and conductive glass wafer. This device can be referred to as a photo supercapacitor or solar capacitor.

Due to its more compact structure, fewer wiring requirements, and shared substrate and electrodes, the proposed device may have higher volumetric and gravimetric energy densities compared to a solar power system composed of separate components. In addition, the fabrication of this device involves the integration of multiple solar cells and SC fabrication technologies, allowing for the combining and simultaneous execution of some similar fabrication operations. This reduces the overall number of operations required compared to the separate manufacture of the constituent elements of the device. The integration of solar cells and supercapacitors into a single hybrid device, in which energy harvesting and storing units are combined into one system, is expected to meet the rising demand for green energy and the miniaturization of wearable devices.

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Versatile Organic Electrochromic Energy-Storage Materials and Devices Based on Nonylbithiazole, 3,4-Ethylenedioxythiophene and Gold Nanoparticles

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Considering the limited natural energy and mineral resources, it is noteworthy that recent technological advancements have focused on electrochemical energy storage systems to produce versatile, affordable, lightweight, renewable organic materials. Energy storage devices, called electrochemical capacitors or organic batteries, stand out with their fast charging/discharging, long cycle life, and being environmentally friendly and safe. It is thought that the structure of D-A type conjugated polymers with tunable structures will provide the basis for new ideas for developing new polymeric material with high energy density and stability. Conjugated polymers that contain donor (D)-acceptor (A) structures together have become one of the important scientific research topics thanks to their adjustable electronic energy levels. In order to design narrow band gap polymers with tunable HOMO and LUMO levels, the optimal sequence can be created by alternating sequences of D and A units. Polymer films prepared in this way will also respond in different colors during the doping and dedoping process. For this purpose, along with increased capacity, energy, and power densities, functional devices to be prepared from materials with both electrochromic and capacitive properties are at an important point in the literature [1,2].

In this study, homopolymer of previously synthesised symmetric molecule [3,4] containing nonylbithiazole (NBT) as the acceptor and ethylene dioxidethiophene (EDOT) as the donor groups (E2-NBT)(Figure 1a), and copolymer with EDOT (n:n, 1:1) were deposited electrochemically on ITO. The electrochemically active polymer (PE2-NBT) (Figure 1b) and copolymer (P[E2-NBT-co-EDOT]) show color changing between charge and discharge states (Figure 1b-inset). According to galvanostatic charge-discharge (GCD) measurements of the PE2-NBT film show a capacity of 57 F/g and 80% capacity retention after 250 GCD cycles (Figure 1c-d). Au nanoparticles were electrochemically deposited onto the surface of the PE2-NBT and P[E2-NBT-co-EDOT] films in order to improve their stabilities. The structure and surface analyzes of the films were investigated via FTIR, scanning electron microscopy (SEM) and atomic force microscopy (AFM) (Figure 1e) measurements. The present study provides insights into the importance of future multifunctional technologies and next-generation energy storage applications that can be possible by the idea of electrochromic polymer films.

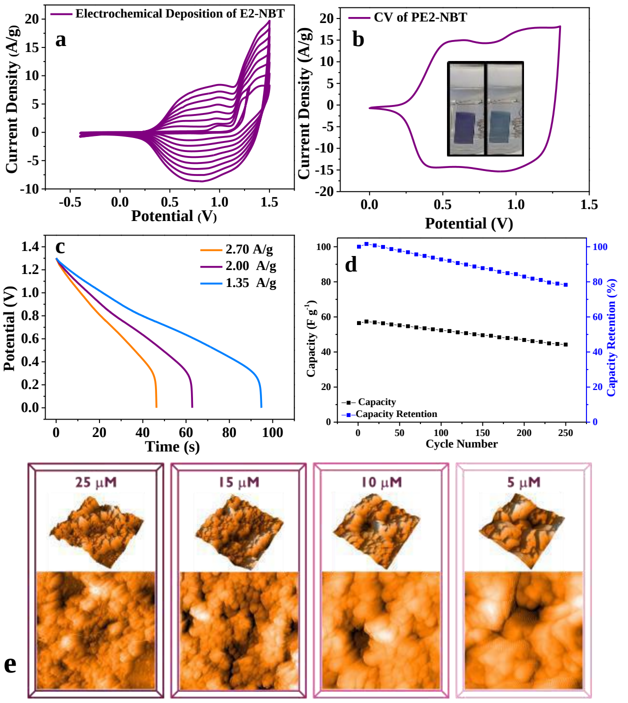

Figure 1. The electrochemical deposition of 1 mM E2-NBT on ITO, in 0.1 M $TBABF_4$ /DCM **(a)**, CV **(b)**, GCD cycle at different current densities **(c)**, GCD stability **(d)**, the AFM images **(e)** of PE2-NBT.

Acknowledgements

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Hysteresis effect reduction in printed and flexible perovskite solar cells with SnO_2 quantum dot-based electron transport layers

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With a power conversion efficiency (PCE) of more than 25%, perovskites solar cells (PSCs) have shown an immense potential application for solar energy conversion. Owing to lower manufacturing cost and facile processibility via printing techniques, PSCs can easily be scaled up to an industrial scale. Printed and flexible PSCs fabricated on lightweight plastic substrates are forecasted to make several viable commercial applications in emerging new technologies such as smart buildings, wearable and portable optoelectronics, the internet of things, and automobile industry [1,2]. The PCEs of flexible and printed PSCs have been improving steadily with the advcnacment and optimisation of printing techniques and processes. SnO_2 is frequently used as an effective ETL material for printed and flexible PSCs due to its excellent electronic and optical properties as well as its exceptional chemical stability [3]. In this work, a synthesis and application of SnO_2 quantum dots (QDs) to prepare ETLs of printed and flexible PSCs is demonstrated. SnO_2 QDs are synthesized via a solvothermal method and processed to obtain aqueous and printable ETL inks [4]. Printed and flexible PSCs are manufactured using a slot-die coating technique employing thin plastic substrates with a transparent condcutive oxide layer (see Figure 1).

Devices are printed in an ambient atmosphere at 25 °C and relative humidity of 40-60%. The printed SnO_2 QDs ETLs are subsjected to UV-light treatment for different time durations and then used to print the remaining device layers except for the top metallic contacts. The behaviour and performance of the obtained devices are investigated using standard characterization techniques. It is found that the UV-treated devices have improved perfromance and reduced hystersis. The underlying reasons for these changes are investigated employing both experimental and theoretical analysis methods. The obtained results provide with a valuable understanding of the effect of SnO_2 QD-based ETLs and their processing on the behaviour and performance of printed and flexible PSCs.

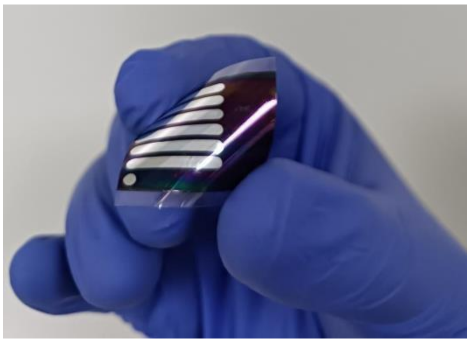

Figure 1. Photograph of a printed and flexible perovskite solar cell with SnO_2 QD-based ETL.

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Design of Highly Selective 2-D Plasmonic Hydrogen Sensors by Tunable Porous Metal Oxide Layers

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Hydrogen economy is a zero-carbon emission economic model that encopasses various subtopics such as hydrogen storage, production, utilization, and detection, with hydrogen being the main energy carrier. This model holds great potential for our future due to several characteristics: the ability to produce hydrogen using renewable energy sources, three times higher energy density compared to fossil fuels (128 MJ/kg), and the production of water as a by product when used in fuel cells. However, hydrogen is an explosive gas when its concentration exceeds 4% in the air. Therefore, hydrogen sensors play a critical role in ensuring the safe use of hydrogen.

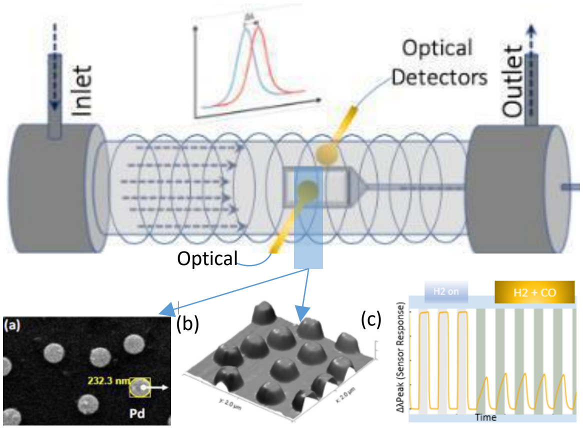

Figure 1. Reactor geometry and measurement principle. (a) SEM image of Pd nanodiscs, (b) AFM image of Pd nanodiscs, (c) plasmonic readouts of Pd nanodiscs on H_2 and H_2+CO environments.

Palladium-based plasmonic hydrogen sensors have gained attention in recent years due to their fast response times even at low hydrogen concentrations. Although they exhibit exellent response time due to intreaction betweem palladium and hydrogen at room temperature and strong plasmonic properties at nano scale, they have some drawbacks. Many studies have done to overcome its disadvantages. Hysteresis formation during hydrogen absorbtion and desorption, sensor deactivation because CO, are significant challenges that need to be overcome for selective and durable usage of the sensors. Binary and ternary Pd alloys, such as PdAu, PdCu and PdAuCu, formed in different concentrations, have been successful in suppressing hysteresis during hydrogen absorption and desorption[1]. The most notable study on sensor deactivation and cross-sensitivity has been conducted using polymeric membranes such as PMMA and PTFE[2]. Althoug the prapered membranes have shown selectivity, particularly in terms of deactivation, hydrogen sensors are devices that need to operate for extended periods in diverse environments. However, polymeric membranes are not resistant to high temperatures and corrosive enviroments.

The aim of our study is to adress sensor deactivation and cross-sensivity by obtaining a selective structure through the fabrication of mesoporous metal oxide (SiO_2) thin film coatings on Pd nanodisks produced via Hole Mask Colloidal Litography (HCL)[3]. The aim of our study is to adress sensor deactivation and cross-sensivity by obtaining a selective structure through the fabrication of mesoporous metal oxide (SiO_2) thin film coatings on Pd nanodisks produced via Hole Mask Colloidal Litography (HCL), as shown in Figure 1a-b, instead of low resistance polymeric membranes. Mesoporous metal oxide structures are produced using the sol-gel method, and the coatings are applied to using the spin coating technique. The mesopores present in the metal oxide thin film coating depend on various parameters such as precursor source, surfactant type and acid-base balance[4]. Additionally, the RPM, coating time, solution quantitiy during spin coating, as well as calcination temperature and time are parameters that affect the porous structure. By optimizing all these parameters, our goal is to create a selective layer on Pd nanodisks and get optical readouts even on H_2+CO environment, Figure 1c, which only allows the entry of hydrogen molecules.

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Energy saving and energy efficiency: Modern experience in Uzbekistan and foreign countries

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The main feature of the electric power industry the coincidence in time of the processes of production and consumption of energy determines the dependence of the mode of energy production on the mode of its consumption. This means that the demand for energy at each moment of time must be covered in strict accordance with the load schedule of a particular consumer. Such schedules are widely used in the practice of production planning, pricing, operational and technological (dispatch) management.

The choice of a tariff system by the consumer should be determined by the economic feasibility and adjustment capabilities of power receivers. The main ways of regulating power consumption modes at industrial enterprises are the following organizational and organizational and technical measures: the introduction of second and third shifts (at one shift and two shift enterprises); establishment of inter shift breaks (during hours of maximum load of the power system); the introduction of different hours of the beginning and end of shifts of various workshops (relative shift of shifts in time); appointment of different days off for various workshops (especially energy intensive ones); redistribution in time (during the day) of individual energy intensive processes; combination in time (coordination) of repairs of units large electrical receivers; development of a sequence for turning off individual electrical receivers and connecting their own generators (if any at the enterprise). The choice of methods of regulation and methods of its stimulation is determined by regional conditions and the current scheme of organization of the energy market.

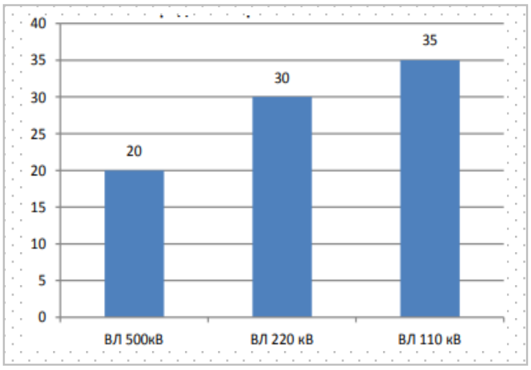

Figure 1. Average age of high voltage networks

The installed capacity of transformers at 35 500 kV substations is about 38,000 MVA. The transmission and distribution system covers the whole country, and 100% of the republic's consumers are connected to the central power supply system. SJSC "Uzbekenergo" has about 5 million consumers.

In the energy industry of the Republic of Uzbekistan, a set of measures has been developed to bring the industry to a new level of development, reduce the energy intensity of electricity generation. The main difference between the program and the previous ones is a radical reform of the electric power industry, the construction of new and modernization of existing generating capacities based on the involvement of best practices and the installation of high tech equipment, which will make it possible to achieve a significant increase in the efficiency of production, transmission and distribution of electric energy. The adopted energy saving program of SJSC "Uzbekenergo" for the period up to 2020 is balanced with the forecast indicators of production and consumption of electrical energy for this period. The program is aimed at realizing the energy saving potential in the industry through the implementation of a system of measures for the efficient use

In view of the foregoing, it can be stated that energy saving and energy efficiency improvement today are important conditions for the development of the Russian economy. Taking into account the various external economic limiting factors, the efficient use of fuel and energy resources is especially relevant for the Republic of Uzbekistan. The accumulated successful experience of foreign countries in energy efficiency policy makes the domestic energy industry move forward, improve and apply new approaches and methods in this area.

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Evaluating the performance of various back-contact designs in perovskite solar cells

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Perovskite solar cells (PSCs) are a highly promising technology in the field of photovoltaic research due to their ability to achieve high (>25%) power conversion efficiencies (PCEs). A typical architecture of PSCs involves a sandwich structure, where a perovskite layer is situated between thin electron and hole transporting layers [1-5]. In recent years, a new back-contact design has been proposed as an alternative architecture for PSCs to further boost their light-harvesting capability and ultimately increase the device efficiency [1-5].

Various designs of back-contact architecture for back-contact perovskite solar cells (BC-PSCs) have been proposed in recent years [1-5]. Based on the design of back-contact electrodes, BC-PSCs can be classified into three main categories: 1) BC-PSCs with quasi-interdigitated electrodes (hereon indicated as quasi-interdigitated back-contact (QIBC) PSCs) [1, 6-9], 2) BC-PSCs with flat-interdigitated electrodes (hereon indicated as flat interdigitated back-contact (FIBC) PSCs) [3, 10], and 3) BC-PSCs with interdigitated electrodes (hereon indicated as interdigitated back-contact (IBC) PSCs) [2, 3, 11].

Back-contact design for the architecture of devices is a promising approach to develop high-performance perovskite solar cells. Here, numerical simulation methods are used to investigate device properties of BC-PSCs with the quasi-interdigitated, flat-interdigitated, and interdigitated electrode designs. The results highlight the principal differences in the designs of the electrodes, and provide an investigation and analysis of the impact these electrodes have on the photovoltaic properties of their BC-PSCs. The effect of the perovskite photoactive layer electronic properties on the performance of BC-PSCs is also investigated. It is revealed that while PSCs with the QIBC design can potentially produce PCEs well above 25%, PSCs with the FIBC and IBC are more tolerant to electronic imperfections in the perovskite layer and can produce PCEs higher than those in devices with the QIBC. Manufacturing and prospective use of electrodes with the QIBC, FIBC, and IBC in developing PSCs are discussed based on the experimental standpoint.

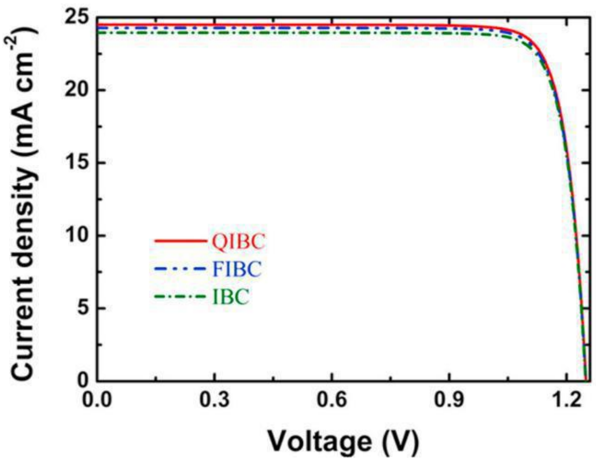

Figure 1. Comparison of the J-V curves of QIBC (red), FIBC (blue), and IBC (olive) PSCs.

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Application of steel slag as sensible thermal energy storage for continuous operation of a waste heat energy reuse plant

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This study analyses the real behaviour of steel slag, a low-cost by-product of electric arc furnaces (EAFs) as thermal energy storage (TES) material, within a waste heat recovery and reuse real industrial environment. Under the scope of LIFE HI4S project [1], a dynamic model of the application has been developed to analyse and optimize the TES system. Solid steel slag particles, in the centimetre range, is used in a 3 m^3 packed bed configuration. Packed bed TES systems have gained significant attention of the research community due to the notable prize increase of fossil fuels.

The thermal properties of steel slag heavily rely on the specific source and process of its origin [2]. This research contributes to the understanding and optimization of steel slag as a viable packed bed TES filler material, considering its interaction, with a given heat source and heat sink. The steel slag used in this project comes from the steelworks of Arcelor Mittal in Sestao (Spain). Figure 1**: thermal properties of the slag. Thermal conductivity (left), specific heat (right)** illustrates the thermal characteristics of the steel slag. These properties and the performance will be assessed, in a waste heat recovery application of the off gas generated in the EAF in this same plant.

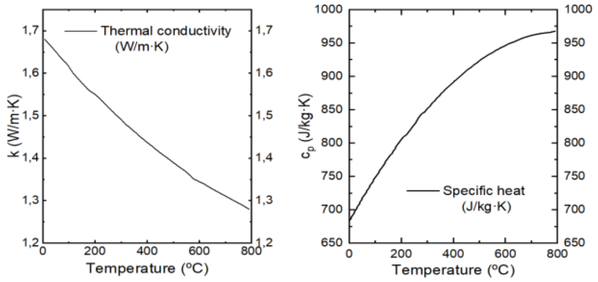

Figure 1: thermal properties of the slag. Thermal conductivity (left), specific heat (right)

As important as the heat recovery is the applicability of the recovered heat. A potential application, addressed in the European-funded project LIFE HI4S [1], is to valorise the captured heat to simultaneously produce a clean heat source to preheat steel scrap and electricity through a low temperature organic Rankin cycle (ORC). To do so, a pilot plant has been designed and is under construction in the aforementioned steelworks.To cope with the intermittency of the gas stream in terms of temperature and availability (EAF is a batch process), the steel slag-based TES is proposed to keep providing energy during low temperature periods or even under periods with lack of heat source The operation temperature range is considered between 385 and 400ºC, the limit temperature of the high temperature filtering system

To design the pilot plant and to scale up the technology a dynamic model has been developed on the software TRNSYS, employing predefined and specific validated subroutines for the packed bed and the scrap pre heating system The model allows the simulation of the thermodynamical behaviour of the preheating scrap on a dynamic environment To assess the benefits of the steel slag packed bed TES, simulations has been performed with and without TES The results of energy and inlet temperature to the preheating are shown in Figure 2.

The results show how the plant is able to get a continuous heat supply at around 400ºC to the scrap during the whole casting even when the off gases are under 385ºC, thanks to the TES increasing the total energy reused in 30 kWh per casting

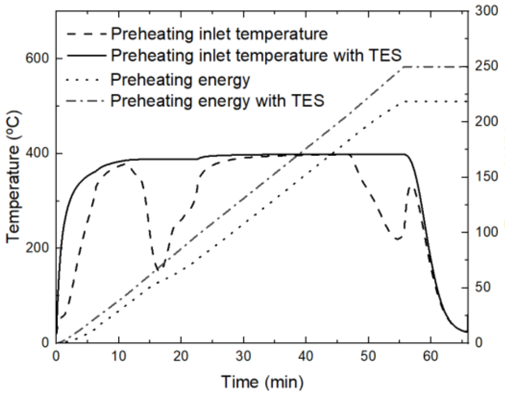

Figure 2 Preheating inlet temperature and reused energy, both with and without TES

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MISCELLANEOUS

The layer-by-layer study of spectral and luminiscent propeties of nanostructures in silicate slide glass

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Silicate glass are widely used in optics. They can be activated by various ions including silver. The introduction of a large concentration of silver in silicate glass is possible by ion exchange (IE) method. Broadband luminescence is an important feature of silver clusters in glass luminescence. A layer-by-layer studies of silver nanostructures after ion exchange haven't been carried out previously. The aim of this work was to investigate spectral and luminescent properties of silver nanostructures in the ion exchange layer of silicate slide glass depending on the stratified surface layer.

Silicate microscope slide glasses were used in this work. Silver clusters were synthesized in glass by IE method at 450 °C for 15-90 min. At each step, absorption spectra of sample were measured. Also, luminescence spectra of sample were measured at an excitation wavelength of 340 nm.

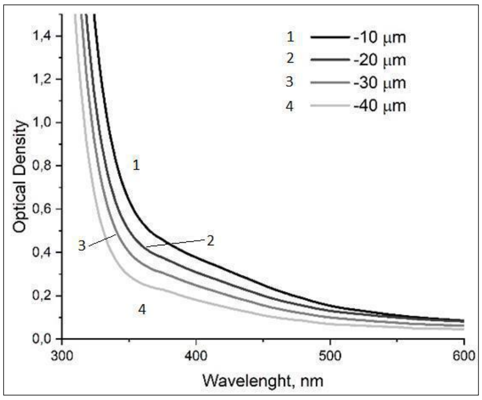

Figure 1. the optical density depending on the stratified surface layer

It was shows that the depth of the silver layer increases from 35 to 55 μm with increasing IE duration time. In each glass, the absorption spectra confirmed the presence of silver nanoparticles with a maximum of about 417 nm. Besides, glass luminesces thankfully to the presence of silver clusters. The luminescence maximum of clusters shifts from 593 to 613 nm because of the presence of different silver clusters set. After chemical etching, the absorption maximum of silver nanoparticles decreases. But a band of remaining silver clusters is revealed. (fig. 1) The silver clusters intensity increases under UV irradiation with the increasing of the thickness of etching layer. It may be related to decreasing of concentration of silver nanoparticles. [1].

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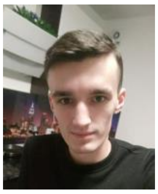

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PEDOT:PSS modified graphite electrodes developed for electrochemical monitoring of interaction between cyanotoxin and DNA

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Sustainable agriculture is an urgent requirement in the modern era in order to reduce environmental contamination and maximize resource efficacy. Silindrospermopsin (CYN) is a cyanotoxin produced by certain blue-green algae in aquatic environments and can be found in agricultural irrigation water and other water sources. The detection of contaminants like CYN in agricultural water sources is essential for monitoring water quality and ensuring the safety of agricultural products. Investigating the interaction between CYN and DNA can contribute to the efficient management of this contaminant in agriculture and the protection of water quality. The demonstration of CYN's interaction with DNA electrochemically will also shed light on its genotoxic properties.

PEDOT:PSS(poly(3,4ethylenedioxythiophene):poly(styrenesulfonate)) is a conductive polymer widely used in electrochemical applications [1]. In this study, PEDOT:PSS-modified pencil graphite electrodes (PGE) were used to investigate the interaction between CYN and DNA. After modification of the electrode surface by passive adsorption of PEDOT:PSS, DNA was immobilized on the electrode surface [2,3]. Subsequently, the DNA-PGE surface was then immersed in CYN solution to observe the interaction and conduct electrochemical measurements [4]. The experimental method is illustrated in Figure 1.

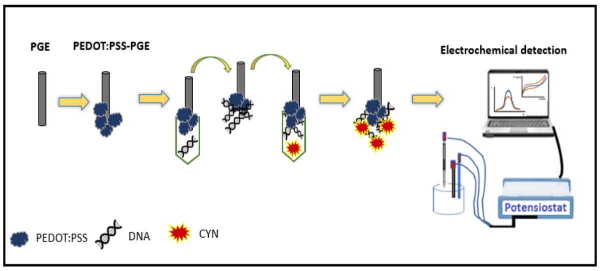

Figure 1. Schematic illustration of the interaction between CYN and DNA at PGE surface.

In conclusion, electrochemical examination of the interaction between CYN and DNA using PEDOT: PSS-modified pencil graphite electrodes was performed for the first time in the literature. This preliminary study of PEDOT: PSS-modified PGE has the potential to revolutionize the rapid and accurate detection of cyanobacterial toxins. These results suggest that this technology can be incorporated into future chip technologies, enabling ubiquitous and efficient toxicity monitoring. It has been demonstrated that a low-cost, disposable, and sensitive toxicity sensor could be developed for environmentally and food-safe sustainable agricultural practices.

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Potential reuse of the Pd-Cu-BTC for reductive sorption of aqueous Hg(II) by thermal desorption technique

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Mercury is a toxic substance that naturally occurs and is present in the environment in several different forms. All forms can have harmful effects on human health, particularly on the nervous system even at their low concentrations. Thus, the World Health Organization (WHO) established the maximum permissible concentration of Hg(II) in drinking water to 1 µg/L [1]. To efficiently treat aqueous Hg(II) several standard water purification methods, including ion exchange, membrane filtration, bioremediation, and adsorption have been studied to date. However, compared to conventional water treatment technologies, catalytic Hg(II) reductive removal has attracted significant attention because of its many positive characteristics including high removal efficiency, fast reduction kinetics, and no headspace Hg(0) formation.

In this study, the Pd-Cu-BTC catalyst was synthesized using the 1,3,5-benzene tricarboxylic acid as an organic support and its reactivity was checked for the catalytic removal of Hg(II) from aqueous solutions. The Pd-Cu-BTC material is characterized using various methods, including scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDS), XPS, X-ray diffraction (XRD) analysis, transmission electron microscopy (TEM), Mercury Porosimetry, and thermogravimetric analysis (TGA).

The kinetic test results showed the Pd-Cu-BTC catalyst reduced Hg(II) to Hg(0) and removed all the species at a reaction time of 2.5 min. The mercury speciation has been examined for the reuse of the catalyst by thermal desorption technique. Since more than 60% of the solid Hg(II) was converted to solid Hg(0) during the reaction, the concentration of Hg(0) on the catalyst surface increased as the reaction time progressed. Other noble metals such as Pt and Ru-impregnated catalyst was studied, however, Pd-Cu-BTC was the best in terms of reactivity and Hg(0) reductive sorption. No headspace Hg(0) formation was observed during the reaction. The experimental conditions such as pH of suspension, catalyst loading, and Hg(II) concentration have been optimized.

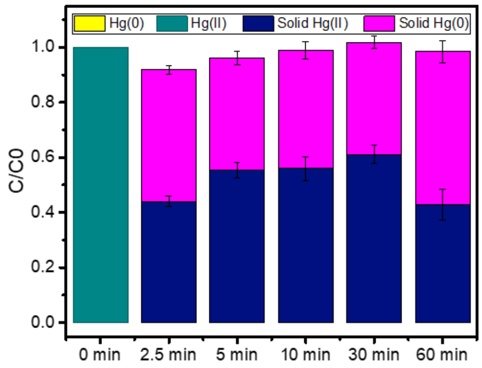

Figure 1. The speciation of solid Hg on the surface of Pd-Cu-BTC.

The experimental results suggest that the reduced Pd-Cu-BTC could be a reactive and feasible catalytic for practical application in water and wastewater treatment to effectively remove aqueous Hg(II) via reductive sorption with enhanced reaction kinetics. The Pd-Cu-BTC can be efficiently reused after thermal desorption at 150ºC for aqueous Hg(II) removal.

Acknowledgments

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Removal of aqueous Hg(II) using ZIF (Zeolitic Immidalozate Framework) derived Co@NC

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Mercury is a hazardous metal that may harm human health, including neurological and renal problems [1]. The World Health Organization states it is one of the "ten leading chemicals of major public health concerns." As a result, 1 ppb was established as the maximum permissible Hg(II) content in drinking water for this contaminant [2]. This chemical's repeated anthropogenic emissions into water bodies are considered a serious environmental issue.

Several sorption, reduction, and filtration-based treatment methods for this contamination were created. Although using sorbents is a promising strategy, it has the drawback of requiring subsequent therapy [2]. Similarly, the fundamental problem with membrane filtration is clogging, plugging, and high operational costs. In this sense, catalytic reduction technologies have addressed many of the abovementioned concerns and limitations. Recently, In-ZVI has shown 99% removal of all Hg species in an aqueous state at neutral conditions [3]. Also, the Zeolitic Imidazolate Framework derived Co@NC has demonstrated high affinity towards gaseous elemental Hg(0) with 85% removal by adsorption on average over 30-240 C [4].

In this work, we have synthesized Co@NC (carbonized ZIF-67) and metal (Ru and Pt) impregnated carbonized ZIF-67 (M-Co@NC) catalysts and tested them for the removal of aqueous Hg(II). The synthesized catalyst was then checked for characterization using the X-ray diffraction (XRD) analysis, scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDS), and transmission electron microscopy (TEM). The test of Co@NC has shown the complete removal of all Hg species at t=2.5 min without the formation of headspace Hg. Then, the Co@NC was tested with Ru and Pt impregnation to identify the best combination of Hg removal and effective reuse. Pt-Co@NC effectively removed all Hg species with a solid Hg(0) portion of about 8% (with 92% Hg(II) adsorbed). After impregnating Ru to Co@NC and reducing the catalyst with NaBH4 before the reaction, the Hg was removed entirely from the aqueous solution with the Hg(0) sorption of 20% and solid Hg(II) as 80%, showing the best results in terms of reuse of the catalyst.

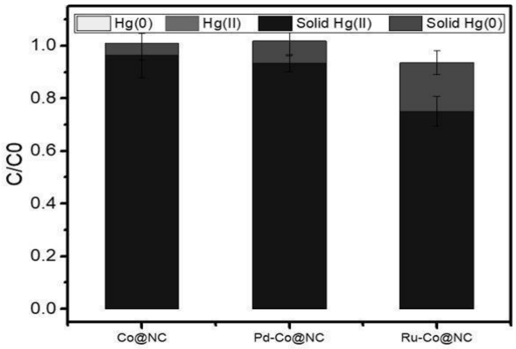

Figure 1. The mass balance results in the speciation of solid Hg on the surface of Co@NC, Pt-Co@NC, and Ru-Co@NC at t=30 min.

The experimental results show that the Co@NC and Ru-Co@NC are very effective materials for removing aqueous Hg(II) using reductive sorption. The catalyst offers high efficiency in completely removing Hg in the aqueous phase without Hg(0) and headspace formation. Also, the catalyst has the potential for its reuse, and future work will be focused on optimizing the necessary parameters to increase the solid Hg(0) concentration on the catalyst's surface to increase its feasibility to further the thermal desorption method at 150 ºC.

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Life cycle assessment (LCA) of water treatment sludge disposal methods

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The water and wastewater sector is responsible for 5% of global greenhouse gas emissions [1]. However, global warming is not the sole environmental issue this sector contributes to – heavy metals contamination of source water and improper utilization of waste (sewage and water treatment sludge) can cause adverse human health impacts.

Most studies that performed life cycle assessments of water supply systems indicate that electricity and chemical consumption are the top contributors in almost every impact category [2]. Yet, the inventory of those studies excluded water treatment sludge characterization and the effect of its disposal, which is usually done by dehydrating and landfilling or direct discharge to the water bodies. Because the former is often associated with additional energy and labor costs, discharge is preferred, especially in developing countries. This study compares the two options to provide the background for cost-environmental impact trade-off decisions.

Almaty and Astana water supply systems were considered for dehydration-landfilling and discharge scenarios correspondingly. Both systems utilize conventional water treatment technologies, including coagulation, flocculation, sedimentation, and disinfection. The plants' operating companies provided the electricity and chemical consumption data, and sludge samples were analyzed using the XRF equipment to obtain detailed sludge content. Identical sludge contents and amounts were considered. Due to the absence of sludge generation rates, the value was estimated using the appropriate literature [3]. The inventory was assembled in the SimaPro 9.4.0.2 software, and energy/materials production-related impacts were taken from the ecoinvent database. The life cycle impact assessment followed the ReCiPe 2016 Endpoint methodology, and the effect was aggregated to a single score value for an adequate comparison.

Table 1. Endpoint impact comparison of discharging dehydrating-landfilling 100 g of sludge.

Damage category	Unit	Dehydration -landfilling	Discharge
Human health	DALY	4,90E-08	4,58E-07
Ecosystems	species. yr	4,05E-11	2,94E-10
Resources	USD2013	2,99E-04	-

As indicated in Table 1, the direct discharge method has 9.34 times more human health impact and 7.23 times more damage to ecosystems than the dehydration-landfilling option. Yet, it has no effect in the resources category as no energy or material inputs are required given that the WTS is discharged to the nearby Ishim River. Such high differences in the human health impact and damage to ecosystems are due to the varying effects of contaminants released to the water and soil media (the top contributors are zinc and arsenic). The aggregated single score results in Figure 1 indicate that direct discharge has a 9.5 times higher impact than dehydration-landfilling.

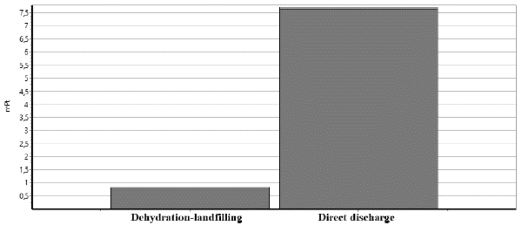

Figure 1. Single score comparison of discharging and dehydrating-landfilling 100 g of sludge.

The results of this study highlight the importance of including the WTS disposal impacts in the inventory of the LCA of water supply systems and suggest choosing the dehydration-landfilling disposal method.

Acknowledgments

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Friction and wear characterization of Si_3N_4 – SiC nanocomposite ceramic

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Abstract:

Friction and wear behaviors of silicon nitride ceramics reinforced by silicon carbide were studied. Friction and wear characterizations of nanocomposites were performed with a reciprocating ball-on-flat tribometer. Tribological tests were carried out with different frequencies and normal loads.
During tribological test, the antagonist was kept stationary and the composite specimen was on tangential cyclic motion using a crank system driven by an electric motor. Tangential force was measured by a load cell placed between the specimen holder and the crank slider system. A data acquisition system stored the output of the load cell. Before each test, the ball and the specimen surfaces were cleaned with ethanol then dried.

The tribometer generate linear reciprocating sliding motion between the contacting bodies. The chosen displacement amplitude for experimental tests was ±5 mm which give a sliding distance of 20 mm for each cycle. Tests were carried out under three different frequencies 0.25 Hz (i.e., 4s cycle duration), 0.75 Hz (i.e., 1.33s cycle duration) and 1 Hz (i.e., 1s cycle duration) who's the corresponding sliding velocity were 5 mm/s, 15 mm/s and 20 mm/s respectively. After each test, ZEISS Scanning Electron Microscope was used to observe wear tracks on the surface of specimens. The cross-section S (mm^2) of the wear groove was calculated from the established surface profile using SJ-210 Hand-held Roughness Tester. Experimental results have shown that tribological behaviors depend on normal load and sliding velocity. Specific wear rate decreases as the frequency increase. The lower friction coefficient is noted for 17N as normal load and 1 Hz frequency which is equal to 0.42 while the highest is noted at 0.25 Hz and equal to 0.92 at 33 N as normal.

The experimental results have shown also that:

- Normal load and sliding velocity have a significant influence on friction coefficients of tested materials.
- Friction coefficient increase with normal load from 0.36 to 0.55. The COF decrease with the increase of frequency from 0.9 to 0.45
- For 0.25 Hz frequency, friction coefficient is equal 0.93 which is very high and unacceptable by the most part of sliding contact.

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X_2FeSi Heusler alloys: A Promising Class of Magnetic Materials

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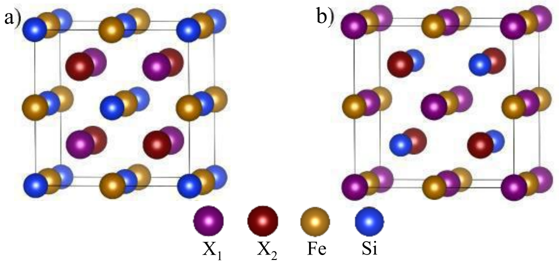
Heusler alloys, named after Fritz Heusler, are intermetallic compounds characterized by a cubic crystal structure. These alloys exhibit remarkable properties such as high spin polarization, shape memory effect, and excellent magnetocaloric properties. X_2FeSi Heusler alloys, where X represents various transition metals, have attracted particular interest due to their unique combination of magnetic and thermodynamic features.

The characteristics associated with electricity and magnetism in X_2FeSi Heusler alloys, possessing full ($L2_1$) and inverse (*XA*) crystal structures with X as Mn or V, have been investigated utilizing density functional theory (DFT). Three distinct calculation methods, namely LDA, GGA, and SCAN, were employed to examine the energy stability of the $L2_1$ and *XA* structures for these alloy compositions. The results indicate that the *XA* structure is energetically stable for both crystal structures. The choice of the functional method does not significantly influence the energy stability of the phases. Notably, the meta-GGA (SCAN) functional more accurately characterizes the electronic properties of these alloys. Through the calculations, it was determined that these compounds exhibit semimetallic behavior. An analysis from a local environment perspective was conducted to comprehend the causes behind the semimetallic band gap and the observed variations in electronic and magnetic properties in Heusler compounds. These findings align with the Slater-Pauling rule for the *XA* structure.

Crystal Structure:

X_2FeSi Heusler alloys crystallize in the face-centered cubic (*fcc*) structure, with X and Fe occupying the tetrahedral and octahedral interstitial sites, respectively, while Si atoms occupy the body-centered position. This arrangement leads to an ordered crystal structure and facilitates the manipulation of magnetic properties by adjusting the elemental composition.

Figure 1 illustrates the crystal structure of Heusler compounds, showcasing both the regular structure ($L2_1$) in Figure 1a and the inverse structure (*XA*) in Figure 1b. These structures correspond to X_2FeSi alloys, with X representing either Mn or V.



Magnetic Properties:

One of the key characteristics of X_2FeSi Heusler alloys is their tunable magnetic behavior. The presence of transition metal elements contributes to the inherent magnetism in these materials. The spin-dependent electronic structure of Heusler alloys results in high spin polarization, making them ideal candidates for spintronics applications. Moreover, X_2FeSi alloys exhibit a range of magnetic ordering, including ferromagnetic, ferrimagnetic, and antiferromagnetic, depending on the composition and atomic arrangement.

X_2FeSi Heusler alloys offer vast potential for various technological applications, including spintronics, magnetic storage devices, sensors, and energy conversion systems. Their exceptional magnetic properties, coupled with the ability to manipulate their crystal structure, make them promising candidates for next-generation electronic devices. For instance, these alloys have shown promise in spintronic devices, such as magnetic tunnel junctions, where high spin polarization is required for efficient spin injection and detection.

Despite the significant progress in understanding X_2FeSi Heusler alloys, several challenges remain. Further research is needed to optimize the alloy compositions, enhance their structural stability, and improve the reproducibility of their magnetic properties. Additionally, exploring novel synthesis techniques, such as thin film deposition and epitaxial growth, could facilitate the integration of these materials into practical devices.

X_2FeSi Heusler alloys represent a promising class of magnetic materials with tunable magnetic properties and potential applications in various fields. The ability to control their crystal structure and tailor their magnetic behavior makes them highly versatile for next-generation spintronic and magnetic storage devices. Further research and technological advancements are expected to unlock the full potential of X_2FeSi Heusler alloys and drive their integration into advanced electronic systems.

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