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

Tuncay Erdil[1] and Cigdem Toparli[1]
[1]Middle East Technical University, Faculty of Engineering, Department of Metallurgical and Materials Engineering, Ankara, Turkey

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.

References

[1].Zhou, Y. et al. Strongly correlated perovskite fuel cells. Nature 534, 231-234 (2016).

[2]Seh, Z. et al. Combining theory and experiment in electrocatalysis: Insights into materials design. Science 355, (2017).

[3]Liu, X. et al. Utilizing solar energy to improve the oxygen evolution reaction kinetics in zinc–air battery. Nature Communications 10, (2019).

[4]Wei, C. et al. Recommended Practices and Benchmark Activity for Hydrogen and Oxygen Electrocatalysis in Water Splitting and Fuel Cells. Advanced Materials 31, 1806296 (2019).

[5]Zhang, L., Cai, W. & Bao, N. Top-Level Design Strategy to Construct an Advanced High-Entropy Co–Cu–Fe–Mo (Oxy)Hydroxide Electrocatalyst for the Oxygen Evolution Reaction. Advanced Materials 33, 2100745 (2021).

Tuncay Erdil completed his bachelor's degree from Middle East Technical University at the Metallurgical and Materials Engineering Department. He is currently a master's student and a research assistant in the same department working on developing bifunctional oxygen electrocatalysts in the Electrochemical Energy Materials Laboratory under the supervision of Dr.Cigdem Toparli.

Presentating author: Tuncay Erdil, e-mail: tunerdil@metu.edu.tr tel: (0312)2105829