

Role of Ni and Fe redox activity in electrochemical properties of O3-NaFe_{1-x-y}Ni_xMn_yO₂ materials as cathodes for Na-ion batteries

Vitalii Shevchenko^{1,2}, Iana Glazkova¹, Daniil Novichkov¹, Irina Skvortsova², Alexey Sobolev¹, Artem Abakumov², Igor Presniakov¹, Oleg A. Drozhzhin¹, Evgeny Antipov^{1,2}

¹Department of Chemistry, Moscow State University, 119991 Moscow, Russia

²Center for Electrochemical Energy Storage, Skolkovo Institute of Science and Technology, Nobel Str. 3, 143026 Moscow, Russia

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_yO₂ cathode materials are an excellent alternative to Li-containing layered oxides such as LiCoO₂ and its derivatives [1]. These compounds are isostructural to α -NaFeO₂ (s.g. R $\bar{3}m$) with Ni, Fe, and Mn in NaNi_{1/3}Fe_{1/3}Mn_{1/3}O₂ being in the 2+, 3+, and 4+ oxidation states, respectively. The possibility of using Fe³⁺/Fe⁴⁺ 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·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 ⁵⁷Fe 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}O₂. 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 $x \approx 0.25$ in Na_{1-x}Ni_{1/3}Fe_{1/3}Mn_{1/3}O₂. Further (de)sodiation includes oxidation of both Fe³⁺ and Ni³⁺. In addition to nickel and iron cations oxidizing to M⁴⁺, a part of iron transforms into the “3+ δ ” state owing to the fast electron exchange Fe³⁺ + Fe⁴⁺ \leftrightarrow Fe⁴⁺ + Fe³⁺. This process freezes upon cooling the material to 35 K, producing Fe⁴⁺ 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_yO₂ (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_yO₂ material accelerates capacity

degradation, on the other hand high content of Fe increases the average discharge potential of material.

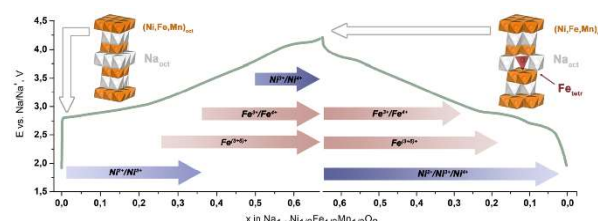


Figure 1. Redox transformations of Fe and Ni cations in O3-Na_{1-x}Ni_{1/3}Fe_{1/3}Mn_{1/3}O₂ during charge/discharge.

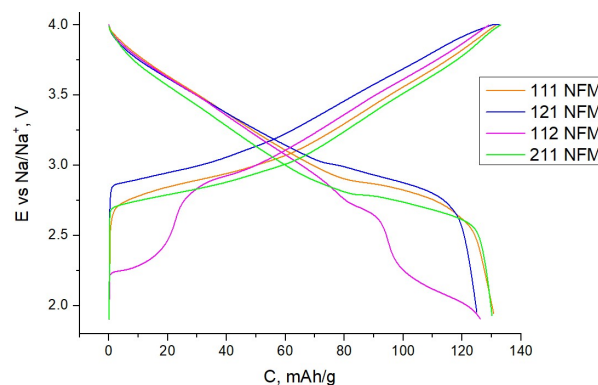


Figure 2. Charge-discharge curves of O3-type NaNi_{1-x-y}Fe_xMn_yO₂ cathode materials.

Acknowledgements

This work was supported by the Russian Science Foundation (grant no. 17-73-30006).

References

- [1] Yabuuchi, N. et al. J. Electrochem. Soc. 2013, 160, A3131–A3137
- [2] Shevchenko, V. et al. Chem. Mater. 2023, 35, 4015–4025



Vitalii Shevchenko obtained his specialist degree in fundamental and applied chemistry in 2018 in department of Chemistry, Moscow State University (MSU). Currently, Vitalii is a junior researcher at Moscow State University and Ph.D student of Skolkovo Institute of Science and Technology.

Vitalii Shevchenko, e-mail: Shev110195@rambler.ru tel: +79899084471