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Reports From The Frontier-Strategies to Design Stable Layered Oxide Cathodes for Na-Ion Batteries

To cite this article: Scott Cushing *et al* 2022 *Electrochem. Soc. Interface* **31** 57

Reports from the Frontier

edited by Scott Cushing,
Interface *Contributing Editor*

This feature page is intended to let ECS award winning students and post-docs write a primary-author perspective on their field, their work, and where they believe things are going. This month we highlight the work of Muhammad Mominur Rahman, the Battery Division 2021 Student Research Award winner.

Strategies to Design Stable Layered Oxide Cathodes for Na-Ion Batteries

by Muhammad Mominur Rahman and Feng Lin

Li-ion batteries are ubiquitous in our lives, as they are used in many modern technologies. Li-ion batteries have dominated the market because of their high energy density and stability. However, sustainability is a big issue with Li-ion batteries, because many of these batteries utilize expensive and/or toxic materials such as Li, Ni, and Co.[1] Hence, researchers have been actively working on developing alternatives to Li-ion batteries. One facile way of developing beyond Li-ion batteries is to replace the Li with more affordable Na. However, with the lower redox potential of Na^+ and its higher density relative to Li^+, Na-ion batteries provide inferior energy density than their Li-ion counterparts. Furthermore, Na-ion batteries suffer from stability issues because of the complex structural and chemical evolutions during battery cycling. Still, Na-ion batteries attract much attention because of cost effectiveness as they require relatively cheap components such as Na, cathodes without expensive elements such as Co and Ni, and an Al current collector instead of Cu. These advantages mean Na-ion batteries can be an attractive choice for large-scale energy storage such as grid energy storage.[2]

Layered oxide materials are widely studied as cathode candidates for Na-ion batteries. They are made of alternating layers of transition metal oxide and alkali ions such as Na (Fig. 1a). Na-layered oxides show intriguing structural and compositional complexities.[3] Unlike their Li-layered counterparts, Na-layered oxides can incorporate many different low-cost transition metals such as Cu and Fe[4] and can be synthesized with different layered structures (e.g., O3, O2, P3, P2).[3] This versatility opens multiple avenues to explore for stable cathode materials for Na-ion batteries. Here, three strategies to design stable Na-layered oxide cathodes are discussed. Taking advantage of their compositional and structural flexibility, stable Na-layered oxide cathodes can be synthesized by 1) utilizing doping chemistry to manipulate the structural and chemical properties, 2) tuning the elemental distribution to optimize the surface and bulk chemistry, and 3) exploring the elemental/compositional space to design stable Na-layered oxide cathodes.

Doping Chemistry to Stabilize Layered Oxide Cathodes

Doping Na-layered oxides with trace elements enables controlled modification of the properties of these materials. Further tunability can be achieved when lattice site-specific doping is performed. For example, Mg can be doped either in the transition metal site or in the alkali-ion site of the layered oxide (Fig. 1a). If Mg is sitting on the transition metal layer, it can suppress local structural distortion,[5] or when it is sitting on the alkali-ion layer, it can act as a pillar against interlayer gliding.[6] Ti doping in layered oxides enables better retention of lattice oxygen during cycling due to strong Ti-O bonding.[7] Doping with both Mg and Ti enables synergistic utilization of their stabilization effects on layered oxide cathodes. For example, doping $Na_xLi_yMn_{1-y}O_2$ with Mg and Ti enables suppression of Jahn-Teller distortion and better overall oxygen retention.[8] Li in $Na_xLi_yMn_{1-y}O_2$ allows access to a large capacity from the material through oxygen redox because of the formation of unhybridized O2p orbitals. Mg-Ti dual doping in this material leads to suppressed Mn dissolution, prevention of Li loss, stabilization of the lattice structure, and reversible redox reaction during cycling (Fig. 1a). Overall, this leads to stable electrochemical performance of Mg-Ti dual doped $Na_xLi_yMn_{1-y}O_2$.

Tuning Elemental Distribution in Cathode Particles

Layered oxide cathodes contain multiple transition metals (TM) with different degrees of hybridization between TM3d and O2p orbitals. Cathode particles interact dynamically with the electrolyte during cycling. Incompatibility of electrolyte with cathode material can lead to electrolyte decomposition, transition metal dissolution, and cathode surface reconstruction.[9,10] During electrochemical cycling, the extent of hybridization of TM3d-O2p orbitals undergoes dynamic evolution, which influences their interaction with the electrolyte. Hence, tuning the TM3d-O2p hybridization can be an

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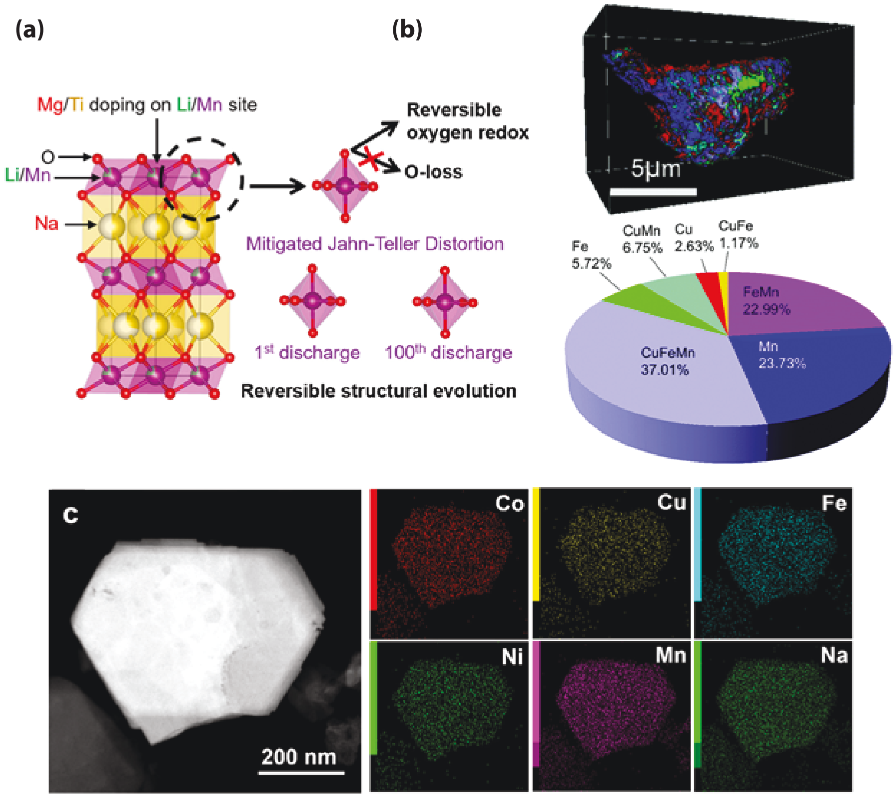

Fig. 1. *Approaches to develop stable layered oxide cathodes for Na-ion batteries. (a) Crystal structure of Na-layered oxides. The structure of these materials is made of alternating layers of transition metal oxides and Na. Doping Na-layered oxides with trace elements such as Mg and Ti in* $Na_xLi_{1-y}Mn_yO_2$ *leads to mitigated Jahn-Teller distortion and reversible structural evolution. Reproduced with permission from Ref. 8. (b) Tuning elemental distribution in individual cathode particles. 3D heterogeneous elemental distribution in* $Na_{0.9}Cu_{0.2}Fe_{0.28}Mn_{0.52}O_2$*. Reproduced with permission from Ref. 11. (c) Exploring the composition space of Na-layered oxides. Elemental distribution in primary particles of* $Na_{0.75}Co_{0.125}Cu_{0.125}Fe_{0.125}Ni_{0.125}Mn_{0.5}O_2$*. Reproduced with permission from Ref. 13.*

effective way of influencing the cathode-electrolyte interaction. Conventionally, layered oxide cathodes are synthesized with a homogeneous distribution of the transition metals. However, our work has shown that the TM3d-O2p hybridization can be tuned by controlling the distribution of transition metals in each individual cathode particle.[11] This approach can lead to an advantageous depth-dependent redox reaction in the cathode particles and thereby influence their interaction with the electrolyte. Taking advantage of these facts, $Na_{0.9}Cu_{0.2}Fe_{0.28}Mn_{0.52}O_2$ with a heterogeneous 3D elemental distribution (Fig. 1b) provides stable electrochemical performance. Hence, our study shows that optimizing the distribution of transition metals in individual cathode particles is an effective way of tuning the electrochemical performance.

Exploring Elemental/ Compositional Space to Design Stable Cathode Materials

One remarkable advantage of a Na-layered oxide is that it can tolerate many different transition metals in its structure because of the large size difference between Na ions (1.02 Å) and TM ions (0.5–0.7 Å).[12] Such flexibility opens opportunities to explore the compositional space of Na-layered oxides, which provides further tuning knobs for performance optimization. This wide design space allows creation of Na-layered oxide cathodes using cheap and abundant transition metals such as Fe. Taking advantage of the vast compositional space of Na-layered oxides, we designed a $Na_{0.75}Co_{0.125}Cu_{0.125}Fe_{0.125}Ni_{0.125}Mn_{0.5}O_2$ cathode material using the majority of the first row transition metals (Fig. 1c).[13] Stable electrochemical performance is achieved with earth-abundant transition metals such as Cu and Fe. Further optimization can be accomplished by designing cathode materials where Cu and Fe are the majority of the transition metals and completely eliminating Co and Ni.

Remarks and Perspectives

Na-ion batteries based on Na-layered oxide cathodes are a promising and cost-effective alternative to Li-ion batteries. Wide compositional variations enable utilization of cheap and abundant elements, which potentially makes them environmentally friendly. Structural and chemical complexities can be exploited to design stable layered oxide cathodes. Incorporating trace elements in Na-layered oxides enables tuning the physicochemical properties of these materials, which further enables performance optimization. Purposefully designing the elemental distribution of cathode particles influences the cathode-electrolyte interaction and takes advantage of depth-dependent redox reactions to stabilize cathode performance. Future development of Na-layered oxide cathodes may combine multiple approaches to controlling elemental distribution along with structural/compositional space exploration to design stable cathode materials.

Acknowledgement

This work was supported by the National Science Foundation under contracts no. DMR 1832613 and CBET 1912885. The authors would further like to acknowledge Virginia Tech College of Science Lay Nam Chang Dean's Discovery Fund for support.

© *The Electrochemical Society. DOI: 10.1149/2.F10224IF*

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