

Innovating Sodium-Ion Battery Cathodes: Enhancing Stability and Performance

Layered metal oxide cathode material engineering for sodium ion batteries holds significant potential for alkali-doped P2 and O3 high-capacity layered oxides.

With the rise in the global reliance on renewable energy sources, the demand for cost-effective, scalable energy-storage solutions has increased. Traditional lithium ion batteries (LIBs), while effective, face resource limitations due to lithium's limited supply and mining complexities. By contrast, sodium (Na) is the sixth most abundant element on Earth, making sodium ion batteries (SIBs) a cheaper, highly safe, and more sustainable alternative for large-scale energy-storage applications (Fig. 1).¹ The performance of SIBs is considerably influenced by the components of the cathode, anode, and electrolyte. However, achieving the energy densities and performance levels of SIBs comparable to LIBs has been challenging, necessitating extensive research into material compositions, structural arrangements, and electrochemical behaviors of Na ion systems. One of the focal points of recent research on SIBs has been the layered P2 and O3 structures in metal oxide cathode materials, which describe how sodium and transition-metal oxides are arranged within the cathode. In this context, “P” indicates sodium ions positioned at prismatic sites, while “O” indicates those located at octahedral sites based on the stacking sequences of oxide layers. The numbers 2 and 3 represent the number of Na ion layers per unit cell. Recently, most researchers have been exploring the ways to modify the layered structures and develop hybrid models to capitalize on each structure's strengths, aiming to suppress the adverse phase transition of layered oxide cathodes. For instance, inserting or doping alkali or transition-metal cations in the layered structure, designing a multi-element intention known as a high-entropy system, and switching between O3 and P2 phases during operation can, in theory, provide the high specific capacities for efficient energy storage and exhibit excellent cycling stability for reliable performance over multiple charge–discharge cycles. Variations of designs remain an area of active investigation, with potential implications for improving SIB performance. Employing a combination of advanced synchrotron X-ray techniques, including X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and X-ray absorption spectroscopy (XAS), plays a key role in examining the structural and electrochemical properties of the layered cathode materials. These techniques allow for in-depth analysis of the materials at an atomic and molecular level, providing insights into their structural stability, chemical composition, and electronic behavior.

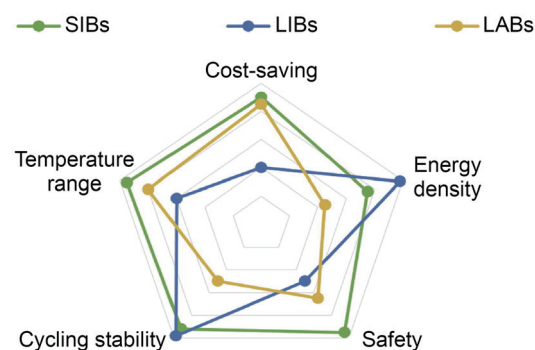


Fig. 1: Comparison of three established rechargeable battery technologies (SIBs, LIBs, and lead-acid batteries (LABs)) in the current market. [Reproduced from Ref. 1]

Most studies have tackled these challenges through innovative cathode material engineering for achieving high energy density and ensuring long-term cycling stability for SIBs. Han-Yi Chen (National Tsing Hua University) focused on a potassium (K)-doped P2-type layered $\text{Na}_{0.67}\text{Mg}_{1/3-x}\text{Cu}_x\text{Mn}_{2/3}\text{O}_2$ oxide cathode, which utilizes alkali-doped configuration to facilitate the movement of Na ions through larger diffusion pathways. This configuration enhances ionic conductivity and improves electrochemical performance.² K ions were selected for doping because of their larger ionic radius compared to Na, which thereby serves as a “pillar” that stabilizes the layered structure during Na ion intercalation and deintercalation. In particular, a doping level of $\text{K}_{0.05}$ showed the most promising results, achieving the highest specific capacity of 203 mAh/g, which represents a significant improvement compared to the undoped material's capacity of 185 mAh/g. This highlights the effectiveness of K doping in expanding ion diffusion pathways and enhancing material stability. *In situ* XRD analysis conducted at **TLS 01C2** provided insights into structural shifts within the cathode materials, revealing that moderate potassium doping (up to $\text{K}_{0.05}$) supports the P2 structure without causing unwanted phase transitions (Fig. 2, see next page). XAS analysis of transition-metal K-edges performed at **TPS 44A** and **TLS 17C1** further supported these findings, revealing that potassium doping did not alter the oxidation states of the transition metals. The structural integrity and charge balance were maintained within the material. This result is critical as it demonstrates that potassium serves as a stabilizer without disrupting the essential redox processes in the cathode material.

Another similar research conducted this year by Ji Liang (Tianjin University, China) explored a Li/Ti co-substitution strategy to address structural challenges in O3-type layered oxide cathodes for SIBs.³ By modifying the local electronic configuration of oxygen in $\text{NaNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ (NM) with an O3 structure, this approach effectively mitigates phase transitions and enhances structural stability, especially at high voltages, a common problem for layered oxides under high sodium extraction. This is a key development in stabilizing O3-phase materials through the specific elemental substitution. It demonstrates that Li/Ti co-substitution strengthens electrostatic bonding in the transition-metal layer and prevents adverse phase transitions, such as those from O3 to OP2, in a voltage range of 2.0–4.3 V. The Li/Ti-modified $\text{NaNi}_{1/9}\text{Ni}_{1/3}\text{Mn}_{4/9}\text{Ti}_{1/9}\text{O}_2$ (LNMT) cathode achieved impressive electrochemical performance with a capacity of 161.2 mAh g^{-1} at 1C and 80% retention after 100 cycles, underscoring the effectiveness of local electronic regulation in addressing phase instability (Fig. 3).

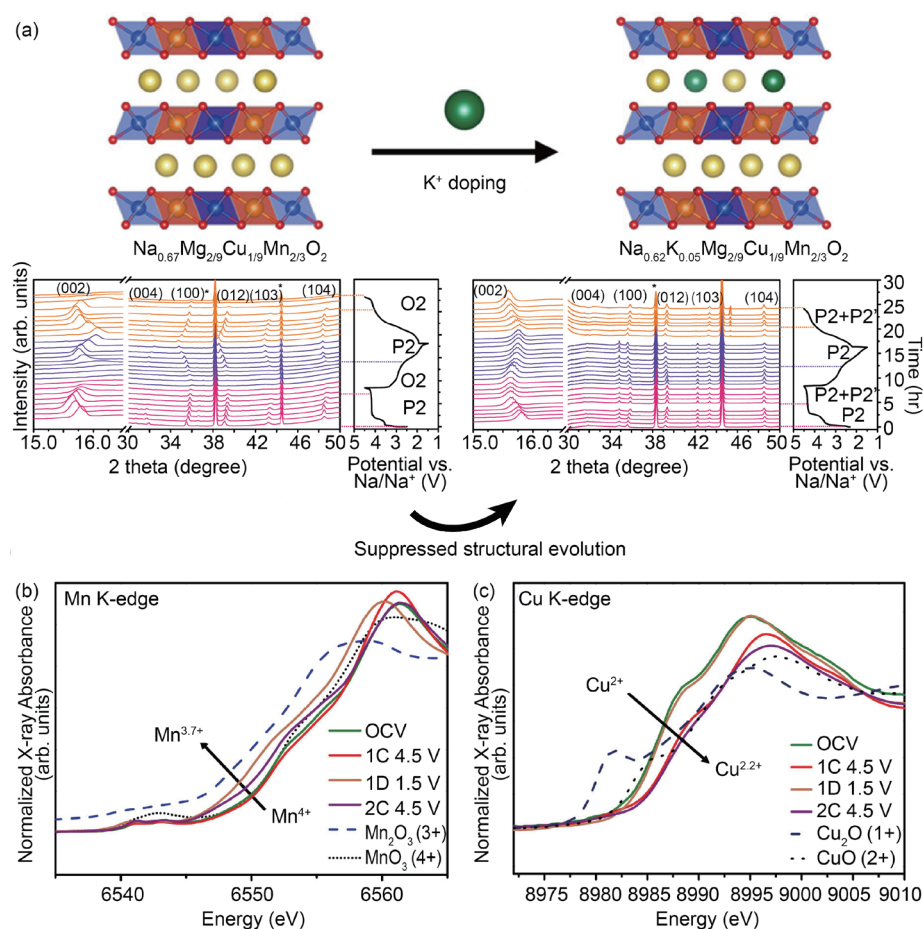


Fig. 2: Schematic K-doped P2 crystal structures and *in situ* XRD patterns of (a) $\text{K}_{0.00}$ and $\text{K}_{0.05}$. *In situ* XAS spectra of (b) Mn K-edge and (c) Cu K-edge of $\text{K}_{0.05}$ during cycling. [Reproduced from Ref. 2]

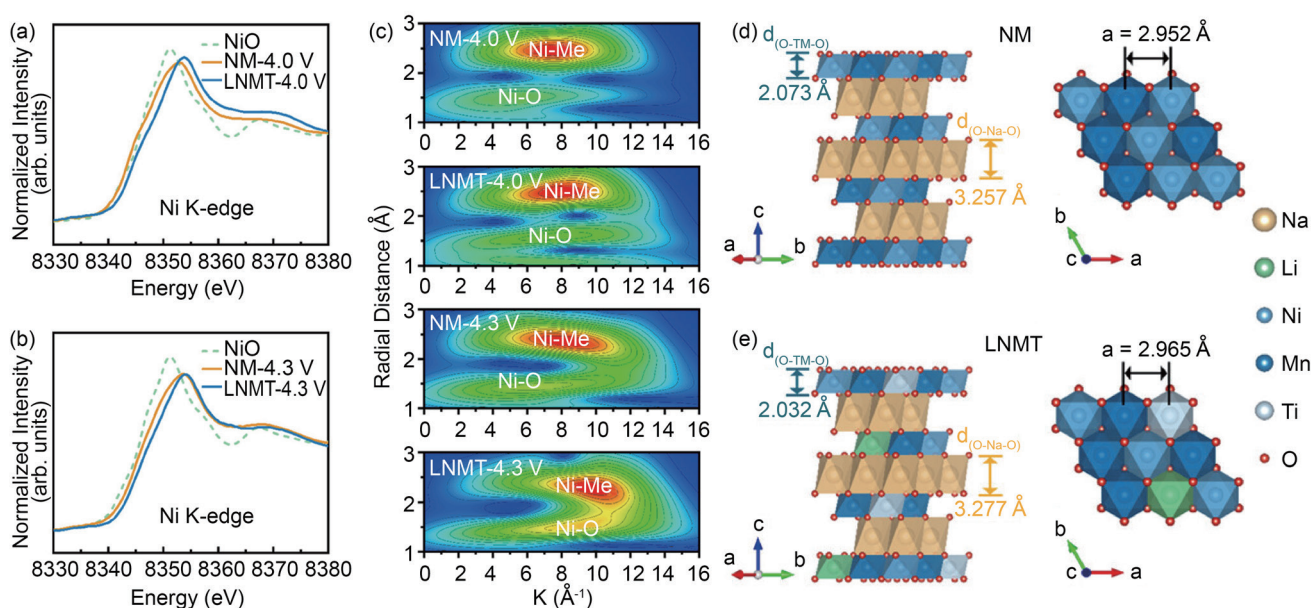


Fig. 3: (a, b) *Ex situ* XANES spectra at Ni K-edge of NM, LNMT, and NiO obtained at different charging conditions. (c) Wavelet transformation diagrams of the NM and LNMT under different voltage states. Schematic crystal structures and detailed lattice parameters of (d) NM and (e) LNMT. [Reproduced from Ref. 3]

XAS analysis conducted at **TPS 32A** revealed that LNMT promotes a stable electronic environment, mitigates drastic structural changes, and supports a more robust charge compensation mechanism. These findings highlight the importance of fine-tuning local electronic and atomic structures in designing high-capacity, high-voltage SIB cathodes. Together, these studies offer key insights into the effects of local structure on the electrochemical behavior of layered oxide cathodes, thereby paving the way for new developments in energy-storage solutions that offer enhanced capacity and cycle life.

In conclusion, while developing high-capacity and long-cycle-life SIBs remains challenging, addressing one of the major limitations of the current sodium ion transport technology in the cathodes highlights the potential of layered structures. Investigating the impact of these layered metal oxide cathodes with complex element compounds could potentially enhance the conductivity, stability, and overall performance. Applying *in situ* synchrotron X-ray techniques is essential for monitoring SIB behavior during operation. These methods provide valuable insights into changes that occur during charge–discharge cycles, enabling researchers to customize materials for improved performance. By combining the strengths of these configurations and leveraging advanced synchrotron X-ray techniques, the research lays the groundwork for more

efficient, durable, and economically viable SIBs. (Reported by Chi-Liang Chen)

*This report features the work of Han-Yi Chen and her collaborators published in ACS Sustain. Chem. Eng. **12**, 12795 (2024), and the work of Ji Liang and his collaborators published in ACS Nano **18**, 18622 (2024).*

TPS 32A Tender X-ray Absorption Spectroscopy
TPS 44A Quick-scanning X-ray Absorption Spectroscopy
TLS 17C1 EXAFS
TLS 01C2 X-ray Powder Diffraction

- XPS, XRD, XAS
- Energy Science, Chemistry, Materials Science, Condensed Matter

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Breathing Zinc–Air Batteries: Clean, Powerful, and Sustainable Energy Solutions

The development of advanced bifunctional catalysts is essential for attaining high-performance cathodes in rechargeable zinc-air batteries.

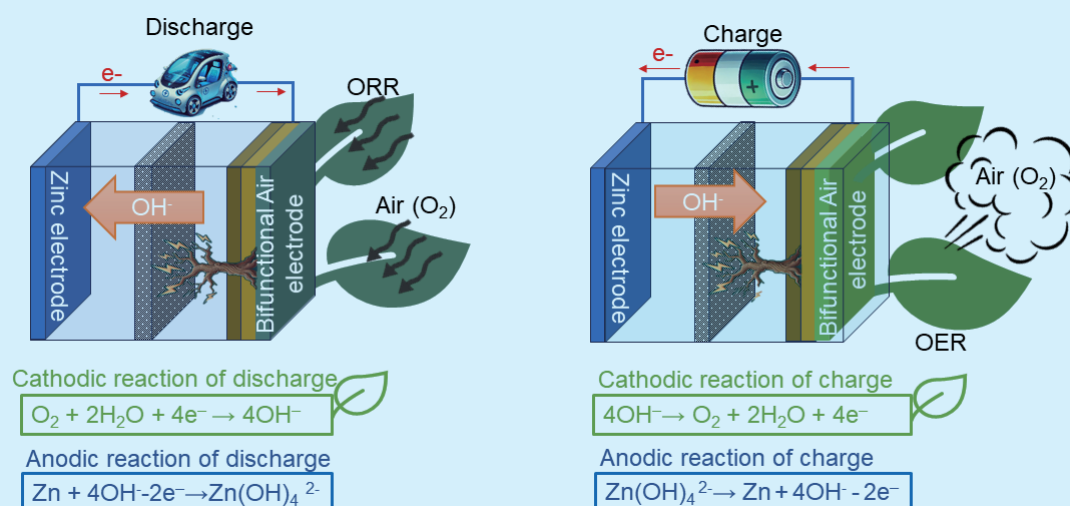


Fig. 1: A schematic configuration of zinc–air batteries and oxygen bifunctional electrocatalysts.