

Review

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Layered oxide cathodes for potassium-ion batteries: challenges, strategies and perspectives

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Abstract

Potassium-ion batteries are currently garnering extensive focus on account of the cost-effectiveness and generous supply of potassium resources. Investigating outstanding electrode materials that exhibit favorable performance is essential for the advancement of these batteries. Layered transition metal oxides have emerged as a highly promising cathode material owing to their high capacity and facile synthesis. However, their effective application is hindered due to inadequate performance, which can be ascribed to irreversible phase transition, air instability and interfacial instability. Herein, this review comprehensively outlines the causes of these three key scientific issues and proposes some corresponding optimization strategies, mainly including element doping, surface modification, structural design, and electrolyte optimization, with the aim of offering insights for the prospective advancement of potassium-based layered oxide cathode materials.

Keywords: Potassium-ion batteries, layered oxides, irreversible phase transition, air instability, interfacial instability

INTRODUCTION

Renewable energy sources such as wind, solar and wave power have recently gained increased attention because of the significant pollution caused by the extensive use of fossil fuels^[1,2]. However, the irregularity



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and fluctuations of these resources impede their direct integration into the grid, resulting in serious resource wastage. Therefore, the establishment of large-scale electrical energy storage (EES) systems is imperative^[3]. Lithium-ion batteries (LIBs) have been extensively utilized in various fields over the recent decades, thanks to their high energy density, superior conversion efficiency, low self-discharge rate and long cycling life^[4]. However, the lithium reserves are restricted (merely 0.0017 wt% of Earth's crust) and distributed disparately across its expanse, causing a sustained increase in the price of Li_2CO_3 , which may further restrict its application in EES and the electric vehicle market^[5]. Compared with lithium, potassium has a relatively high natural abundance (2.47 wt% of Earth's crust) and exhibits similar physical and chemical properties to lithium, establishing potassium-ion batteries (PIBs) as a promising alternative to LIBs. Besides, PIBs have a working principle similar to LIBs by shuttling the K^+ between the cathode and anode^[6-8]. Recently, research on PIBs has received significant interest because of their distinctive properties, which set them apart from both LIBs and sodium-ion batteries (SIBs): (1) graphite can be served as the anode in PIBs, whereas it is not effective for SIBs because Na^+ ions cannot be intercalated into graphite^[9]; (2) K^+ has a smaller Stokes radius, means it exhibits the lowest de/solvation energies among alkali metal ions. The mild interaction of K^+ ions with solvent molecules allows for faster ion transfer and higher ion conductivity, which can stimulate the potential in low-temperature performance^[10,11]; (3) The standard potential for K^+/K , standing at -2.93 V concerning a standard hydrogen electrode, is lower than that of Na^+/Na and is similar to that of Li^+/Li , which is beneficial for higher working voltage^[12]; and (4) Substituting the costly copper foil with aluminum foil as a current collector can contribute to additional reductions in both the overall weight and cost of PIBs^[13].

The electrode materials are crucial in determining electrochemical properties. Anode materials suitable for PIBs can be mainly classified into carbon-based materials (such as graphite, soft carbon and hard carbon), alloys, organic materials and conversion-type anode^[14,15]. Among them, graphite is the most promising anode for PIBs due to its high theoretical capacity (279 mA h g^{-1}) and low cost. However, a large volume variation during potassiation/depotassiation would irreversibly damage the solid electrolyte interface layers, thereby resulting in poor rate performances and cycling stability. In recent years, researchers have made significant improvements in their electrochemical properties by extending the interlayer space of graphite and constructing a coating layer. The incorporation of S/N heteroatoms into graphite nanosheets yielded an expanded interlayer spacing of 0.39 nm, coupled with a high density of structural defects and electroactive sites, which synergistically enabled exceptional cycling stability, retaining a capacity of 142 mA h g^{-1} even after 5,000 cycles at a current density of 0.5 A g^{-1} ^[16]. In sharp contrast to recent progress in anode materials, the low capacity and short cycle life of the current potassium cathode materials fall short of commercial energy density targets, which severely limits the viability of PIBs for grid-scale energy storage. The cathode materials of PIBs mainly include layered transition metal oxides, Prussian blue analogs (PBAs), polyanionic frameworks and organic compounds^[17-20]. PBAs, characterized by their open framework structure, exhibit high capacity and high voltage but suffer from structural instability due to crystal water-induced collapse and low electronic conductivity. Organic cathodes offer high theoretical capacities through multi-electron redox reactions, yet their practical application is hindered by severe dissolution in electrolytes and low operating voltages. Polyanionic compounds leverage robust covalent frameworks to deliver exceptional cyclability and high voltage, though their low electronic/ionic conductivity result in sluggish kinetics causing poor rate performance in PIBs. Motivated by the superior electrochemical performance of layered transition metal oxides in SIBs^[21], layered oxides have also become a research hotspot for PIBs. Compared to other cathode materials, potassium layered oxides exhibit two-dimensional diffusion channels that furnish abundant active sites and expanded spatial accommodation for K^+ (de)intercalation during electrochemical cycling, which contributes to enhanced specific capacity. Furthermore, the incorporation of high redox potential elements such as nickel and cobalt enables the cathode to achieve high working voltage, synergistically enhancing energy density. Additionally, their compatibility with mature synthesis techniques

and low raw material costs render them favorable for scalable production^[22,23]. However, critical challenges also exist. During the K^+ ion insertion and extraction from the cathode, the large radius of K^+ ions leads to severe phase transitions, resulting in poor electrochemical performance^[24]. Besides, the layered oxide cathodes of PIBs generally experience severe structural degradation when exposed to ambient conditions, impairing cell performance and presenting a substantial challenge for material storage^[25]. Furthermore, the Coulombic efficiency (CE) and cycle life are often unsatisfactory in PIBs, which may be related to severe side reactions occurring between the electrode and the electrolyte^[26]. Additionally, the interphase between the cathode and electrolyte is also an important part of ensuring long life cycling^[27]. Interfacial stability is essential for achieving better electrochemical performance.

To date, many approaches have been proposed for the modification of K layered oxides; however, there is currently a limited comprehensive understanding regarding the relationship between degradation mechanisms and optimization strategies. This review addresses these gaps by establishing structure-property-performance relationships from cathode bulk to interphase dynamics, thereby unifying fragmented knowledge into actionable design principles. In this review, the mechanism of the main problems, including irreversible phase transition, air instability and interfacial instability, are discussed. In addition, optimization strategies including element doping, surface modification, structure design and electrolyte optimization are summarized to enhance the electrochemical performance of PIBs. By bridging fundamental degradation mechanisms with scalable engineering solutions, this review provides a roadmap for accelerating PIBs toward commercial viability in EES applications.

STRUCTURE CLASSIFICATION

Layer transition metal oxides typically are composed of edge-shared TMO_6 octahedral layers and alkali layers, which can be given using a simple expression such as A_xTMO_2 ($0 < x < 1$, where A represents alkali metals such as Li, Na, K, *etc.*, and TM indicates transition metal such as Ni, Fe, Mn, *etc.*). Different phases will be formed when TMO_2 layers stack along the c-axis in different ways. Generally, the K layered oxides can be identified as P-type (P2, P3) and O-type (O3), where P denotes K^+ ions in prismatic sites and O denotes K^+ ions occupying octahedral sites, respectively, while number 2 or 3 indicates the number of TMO_2 layers in distinct stacking modes, as shown in Figure 1. In addition, in instances where the structure exhibits slight distortion, a prime symbol (') is incorporated to differentiate it from the original structure^[28-30].

P2-type layered oxides for PIBs are usually regarded as 2H phases with $P6_3/mmc$ space groups, and the K^+ ions are accommodated at prismatic sites with two types of TMO_2 layers: AB and BA^[31]. There are two different sites for K ions in an alkali layer: K_e and K_f , which represent edge-shared and face-shared TMO_6 octahedral, respectively. Because of the large K^+ ion radius and strong coulombic repulsion, the two kinds of K sites usually cannot be occupied at the same time. K^+ ions migrate through 2D prismatic channels accompanied by redox reactions of transition metals during charging and discharging process. Typically, during deep potassium extraction, the P2 phase will transform to O2 phase, which has an AB-AC oxygen stacking sequence, caused by the increased interlayer repulsion of TMO_2 layers. The compressed interlayer spacing and high stress will be generated, accompanied by phase transitions, which greatly influence the specific capacity and cycling life of the cathode^[32].

For P3-type oxides, one of the triangular faces of each KO_6 prism is shared with a TMO_6 octahedron, and the remaining triangular face shares its edges with three distinct TMO_6 octahedra on the opposing side. Differing from the P2 phase, the oxygen stacking sequence in the P3 phase follows the AB-BC-CA arrangement along the c-axis with the $R3m$ space group^[33]. In addition, the P3 phase is usually obtained at a low synthesis temperature, while the P2 phase is typically achieved at a high synthesis temperature, which

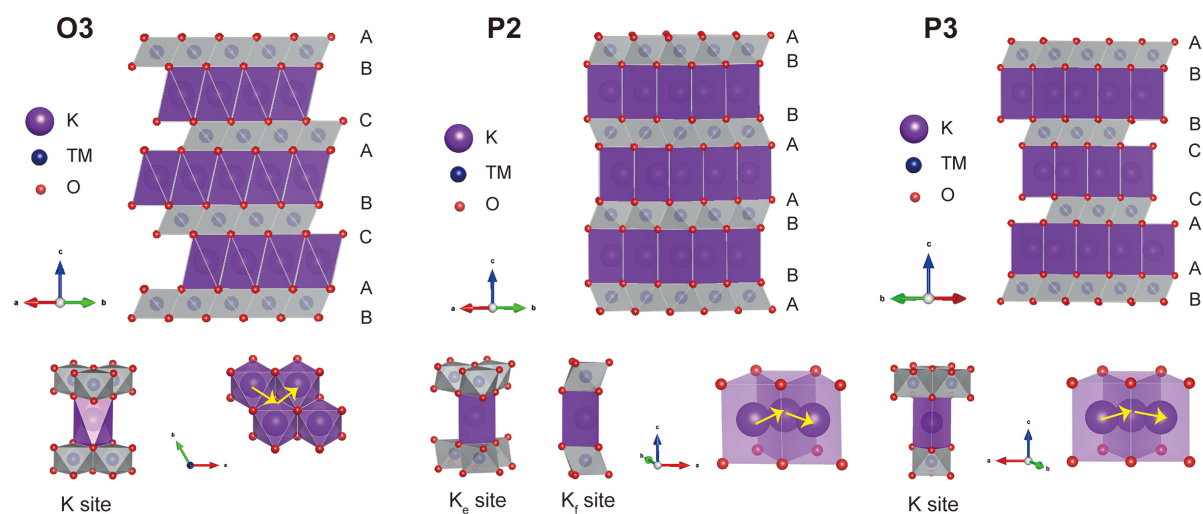


Figure 1. The schematic diagram of structure, K site and diffusion path of O3, P2, P3.

suggests that it is difficult for the P3 phase to transform to the P2 phase during charging-discharging process without breaking TM-O band because of the low energy. In P3-type oxides, the prismatic sites provide more flexible diffusion channels, enabling a smoother K^+ migration with reduced energy barriers. The P3 phase usually transforms to the O3 phase under high voltage operation, caused by the gliding of TMO_6 octahedral slabs by $(1/3, 2/3, 0)$ without breaking TM-O bands^[34]. P-type layered oxides offer high ionic conductivity and moderate capacity but suffer from irreversible phase transitions and interface instability. Structural engineering (e.g., doping, coating) and optimized electrolyte formulations are critical for enhancing their cyclability which will be discussed in detail later.

O3-type layered oxides are usually designed as a 3R phase with $R\bar{3}m$ space group and both transition metal ions and K^+ ions are located within octahedral sites with the oxygen stacking sequence conforming to AB-CA-BC, satisfying a cubic closed packed (ccp) structure^[35]. It is feasible for the O3 phase to transition into the P3 phase. However, the transformation of the O3 phase into the P2 phase or O2 phase through electrochemical potassium insertion/extraction is challenging. The diffusion of K ions entails direct passage through the adjacent trigonal prismatic sites in the P-type phase. In contrast, K^+ ions need to traverse the transitional tetrahedral sites between two adjacent octahedral sites in O-type phase owing to the narrow interlayer spacing, which presents a higher diffusion barrier and slower kinetics^[36].

In PIBs, P-type layered oxide cathodes are more commonly synthesized compared to O-type layered oxides. This preference is linked to the larger ionic radius of K^+ ions, which results in strong electrostatic interactions between ions when they occupy octahedral sites, thereby destabilizing the layered structure^[36]. Among various P-type cathodes, manganese-based layered oxides have emerged as a prominent research focus due to the plentiful supply and low cost of manganese resources. Liu *et al.* synthesize both P2-type and P3-type K_xMnO_2 with potassium contents of 0.3 and 0.45, respectively, which indicates that the potassium content is a crucial factor influencing the formation of different phases^[37]. Moreover, Co-based and Cr-based oxides serve as popular model systems^[38,39]. However, only $KSrO_2$ and $KCrO_2$ have been identified to currently exhibit a thermodynamically stable O3 phase, which was unveiled through the utilization of Density Functional Theory (DFT) to compute the energy above hull for different O3-layered $KTMO_2$ compounds^[40]. Single-transition metal oxides frequently demonstrate multiple phase transitions and limited structural stability when extracting K^+ ions from the alkali ion layer. Harnessing the synergistic

effects of diverse elements usually leads to enhanced performance in cathode materials.

SYNTHESIS METHOD

The development of high-performance layered oxide cathodes for PIBs relies heavily on advanced synthesis techniques to achieve structural stability, phase purity, and optimized K^+ diffusion kinetics. The synthesis procedures for K layered oxides primarily encompass solid-state reactions, sol-gel processes, co-precipitation synthesis, hydrothermal/solvothermal techniques and electrochemical ion exchange. Their respective merits and drawbacks will be critically evaluated in subsequent sections.

The solid-state reaction is the most commonly used method for the preparation of layered oxides. It obtains the product by mixing potassium salts and oxide precursors, pressing them into pellets, and then sintering at high temperatures. The method is facile, but it is difficult to regulate the particle size and morphology. Scanning electron microscopy (SEM) characterization revealed that the as-prepared $P3\text{-K}_{0.5}\text{MnO}_2$ oxide exhibits plate-like morphology with particle sizes ranging from 1 to 2 μm ^[41]. This morphology typically compromises electrochemical performance due to limited interparticle contact areas and insufficient ionic diffusion pathways. Furthermore, the conventional solid-state method fails to ensure atomic-scale homogeneity, leading to detectable impurity phases. A series of $\text{K}_{0.67}\text{Mn}_{1-x}\text{Ni}_x\text{O}_2$ ($x = 0, 0.08, 0.17, 0.33$) cathodes were prepared via solid-state reactions^[42]. Rietveld analysis of the $x = 0.33$ sample confirmed the presence of a NiO impurity phase, which correlates with its inferior capacity retention compared to the $x = 0.17$ counterpart. To address these limitations, advanced atomic-level mixing approaches such as sol-gel synthesis have been proposed.

Sol-gel method involves dissolving metal precursors (such as nitrates or acetates) in a solvent, followed by chelation with organic agents (such as citric acid, ethylene glycol) to form a homogeneous sol. Subsequently, the sol transitions into a gel, which is then dried and calcined at high temperatures to yield target oxides. The sol-gel-derived $\text{K}_{0.7}\text{Mn}_{0.7}\text{Ni}_{0.3}\text{O}_2$ exhibits phase-pure P3-type structure without detectable NiO impurities and superior performance (124.2 mA h g^{-1} at 0.1 A g^{-1} , a capacity retention of 86.2% at 0.5 A g^{-1} after 500 cycles)^[43]. However, sol-gel synthesis is complex, requiring meticulous optimization of pH, temperature, and chelating agent ratios. The method is time-intensive, prone to organic residue contamination, and less scalable compared to solid-state, limiting its industrial applicability. Despite these drawbacks, its capacity to produce high-performance cathodes makes it a preferred choice for lab-scale PIB research.

Co-precipitation synthesis is a solution-based method for preparing layered oxide cathodes for PIBs. This technique involves dissolving transition metal salts (such as sulfates or nitrates) in aqueous solutions, followed by the addition of a precipitating agent (such as NaOH or KOH) under controlled pH and temperature to form homogeneous hydroxides or carbonates. The precipitates are filtered, dried, and calcined with a potassium source to yield layered oxides. Co-precipitation enables uniform particle size distribution and minimizes cation mixing. Peng *et al.* developed hollow $\text{K}_{0.5}\text{MnO}_2$ submicrospheres via co-precipitation method^[44]. SEM imaging reveals well-defined spherical morphology with uniform particle sizes averaging 600 nm in diameter. Thanks to the special structure, the cathode achieves a capacity retention of 89.1% at 200 mA g^{-1} after 400 cycles. It is worth noting that the precipitation agent, pH, stirring speed, and temperature must be carefully adjusted to ensure the quality of the products.

Hydrothermal/Solvothermal Synthesis is also a solution-based technique for fabricating K layered oxide cathodes where precursors react in a sealed autoclave under elevated temperatures and pressures, using water (hydrothermal) or organic solvents (solvothermal) as reaction media. This method enables precise control of nanostructured morphologies, such as nanowires or microspheres, which enhance K^+ diffusion

kinetics. Deng *et al.* synthesized $\text{K}_{0.65}\text{Fe}_{0.5}\text{Mn}_{0.5}\text{O}_2$ cathodes by two different routes (hydrothermal and conventional solid-state reactions) to demonstrate the influence of the synthetic procedure on the properties of the cathode^[45]. The s- $\text{K}_{0.65}\text{Fe}_{0.5}\text{Mn}_{0.5}\text{O}_2$ microsphere was synthesized via hydrothermal method. Conversely, the c- $\text{K}_{0.65}\text{Fe}_{0.5}\text{Mn}_{0.5}\text{O}_2$ was synthesized through the solid-state route. The results show that the s- $\text{K}_{0.65}\text{Fe}_{0.5}\text{Mn}_{0.5}\text{O}_2$ microspheres exhibited superior capacity and durability to the irregularly shaped c- $\text{K}_{0.65}\text{Fe}_{0.5}\text{Mn}_{0.5}\text{O}_2$ particles. Nevertheless, the method requires specialized equipment, poses scalability challenges due to batch processing, and involves longer reaction times. Additionally, solvothermal routes may raise safety and cost concerns with organic solvents.

Electrochemical ion exchange is an advanced method to prepare layered oxide cathodes for PIBs by leveraging controlled voltage or current to drive the exchange of pre-inserted ions (e.g., Na^+) with K^+ ions in an electrolyte medium. This method leverages the structural stability of sodium-based oxides to create stable potassium phases that are challenging to synthesize directly. The $\text{Na}_{0.67}\text{Li}_{0.12}\text{Ni}_{0.22}\text{Mn}_{0.66}\text{O}_2$ cathode was galvanostatically cycled in a cell with the configuration K-metal| KClO_4 in ethylene carbonate (EC):diethyl carbonate (DEC)| $\text{Na}_{0.67}\text{Li}_{0.12}\text{Ni}_{0.22}\text{Mn}_{0.66}\text{O}_2$ ^[46]. The Na^+ ions are gradually substituted with K^+ ions, yielding P2- $\text{K}_{0.56}\text{Na}_{0.11}\text{Li}_{0.12}\text{Ni}_{0.22}\text{Mn}_{0.66}\text{O}_2$. The cathode can operate over a wide voltage range of 1.5–4.6 V, demonstrating excellent high-voltage stability. A systematic comparative analysis by Nathan *et al.* revealed that P2- $\text{K}_{0.7}\text{Cr}_{0.85}\text{Sb}_{0.15}\text{O}_2$ cathodes synthesized through electrochemical ion exchange retain trace sodium content and exhibit better performance than the cathode obtained by solid-state reaction^[47].

CHALLENGES

While K layered oxides exhibit a multitude of advantageous characteristics, their practical application is constrained by suboptimal electrochemical performance, influenced by a combination of factors^[48,49]. Throughout the continuous charge and discharge cycles, the extraction/insertion of larger K^+ ions typically induces volume contraction/expansion, potentially leading to irreversible phase transitions and hastening electrode degradation. Additionally, exposure to air frequently results in a significant decline in cathode performance, largely due to surface reconstruction and K^+/H^+ ion exchange. Interfaces, serving as the primary sites for charge transfer, have an important impact on ion transport and cycling stability. Herein, the fundamental reaction mechanisms underlying these challenges and their association with electrochemical performance will be thoroughly discussed below.

Irreversible phase transition

Irreversible phase transitions commonly occur at high voltage regions because of the alterations in interlayer electrostatic forces during the de/intercalation of K^+ ions. Some phase transitions can have a beneficial impact on layered oxides. For instance, the transformation from O-type to P-type can enhance the diffusion of K^+ ions by bypassing the higher diffusion barrier in tetrahedral sites^[50]. Conversely, irreversible phase transitions are responsible for the decline in electrochemical performance of K layered oxides. Besides, the persistent effects of interfacial stress often lead to the formation of intragranular cracks, which enlarge the contact surface between electrolyte and electrodes, exacerbating side reactions and reinforcing the fatigue of layered oxides^[51].

Layered P3- $\text{K}_{0.5}\text{MnO}_2$ exhibits a high capacity of 140 mA h g^{-1} within the voltage range of 1.5–4.2 V, characterized by two striking plateau features at 3.7 and 4.1 V (vs. K^+/K) during the K^+ extraction. However, these voltage plateaus become less prominent during the subsequent discharge process [Figure 2A]^[52]. Subsequently, a P3-O3 phase transition was revealed by *in-situ* XRD and DFT calculation upon K^+ extraction to 0.41 which is primarily driven by $\text{K}^+/\text{vacancy}$ ordering and sliding of TMO_2 layers [Figure 2B]. The results suggest that the P3-type structure demonstrates minimal energy levels with increased K content,

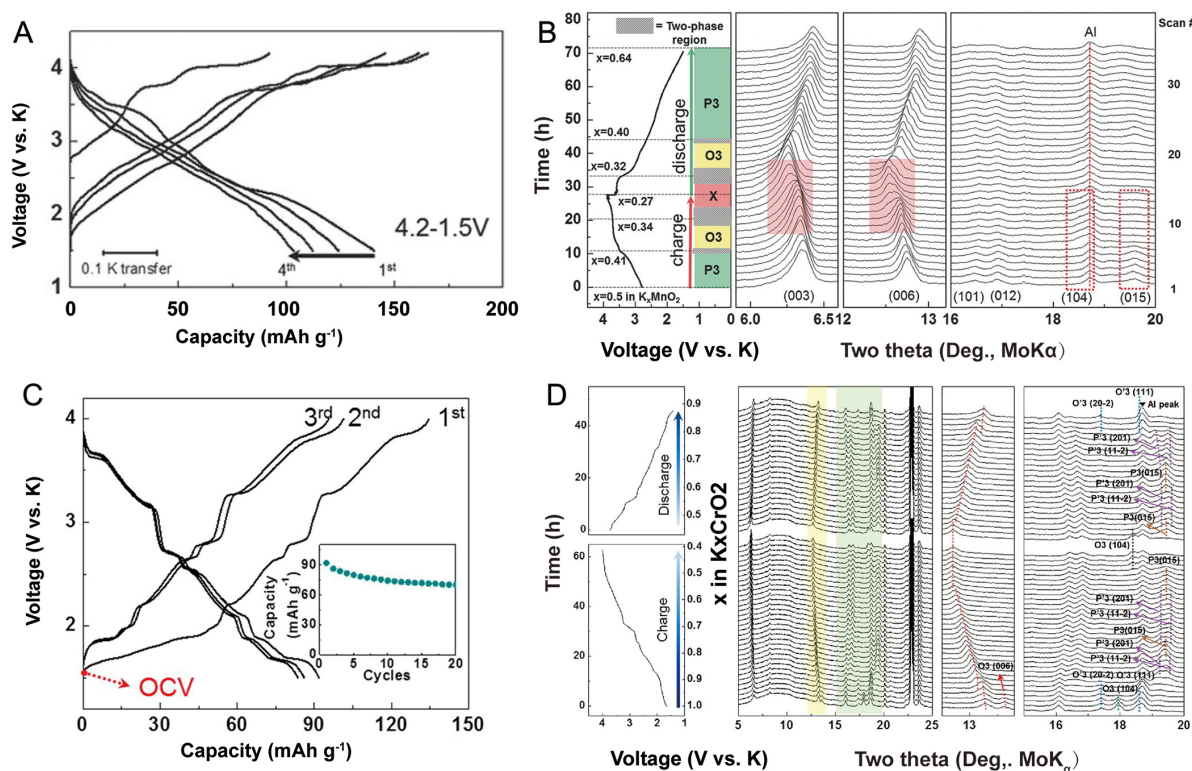


Figure 2. (A) GCD curves and (B) *In-situ* XRD pattern of P3-K_{0.5}MnO₂ between 1.5–4.2 V^[52]. (A and B) Reprinted with permission from Ref. [52]. Copyright 2017 Wiley-VCH [52]. (C) GCD curves and (D) *In-situ* XRD pattern of O3-KCrO₂^[40]. (C and D) Figures reprinted with permission from Ref. [40]. Copyright 2018 American Chemical Society [40].

while the O3-type framework achieves stability with reduced potassium content. Notably, with further extraction of K⁺ ions, a special phase, defined as the X phase, appears, characterized by the (104) peak in the O3 phase and additional characteristic peaks at the left of the (003) and (006) peaks. Unlike P-type cathodes, the O-type cathodes undergo more intricate phase transitions during de/potassium. O3-KCrO₂ delivers an initial discharge capacity of 92 mA h g⁻¹ and retains a capacity of 70 mA h g⁻¹ after 20 cycles at 5 mA g⁻¹ accompanying multiple voltage plateaus, which may relate to the complex phase transitions when the content of potassium changes [Figure 2C]^[40]. The structural evolution, as revealed by *in-situ* XRD, shows a complex series of phase transitions (O3-O'3-P'3-P3-P'3-P3-O3) during the charging process [Figure 2D]. However, the cathode does not revert to its initial O3 phase after discharge, a key factor contributing to its poor cycling stability. The intensity of phase transitions observed in K_xCrO₂ is plausibly related to the interaction between K⁺ ions, necessitating the formation of multiple intermediary phases to mitigate such interactions with increasing potassium content. Interestingly, the authors noted that before the *in-situ* experiments, phase separation occurred within the electrode, attributed to partial K⁺ ion deintercalation after mixing KCrO₂ with carbon.

Air instability

The two-dimensional diffusion pathway in layered oxides is conducive to ion transport; nonetheless, atmospheric molecules such as water and CO₂ can readily infiltrate, triggering detrimental side reactions^[53]. Firstly, carbon dioxide and water molecules adsorbed on the particle surfaces react with the deintercalated alkali metal ions, leading to the generation of surface residual alkali compounds (carbonates, hydroxides, etc.) which are generally harmful because of their poor conductivity, hindering charge transfer between

electrode and electrolyte and causing the deterioration of electrochemical performance^[54]. Secondly, the binder termed poly (vinylidene fluoride) (PVDF) can react with these residuals resulting in the defluorination polymerization of PVDF during slurry preparation^[55]. Besides, the crystal structure is degraded under the influence of atmospheric molecules, leading to irreversible capacity loss. And the air sensitivity of layered oxides poses a significant challenge in commercial utilization as meticulous regulation of annealing and storage environment may result in increased operational costs^[56].

The mechanisms responsible for the poor air stability of layered oxides represent a long-standing topic of contention within scientific discourse^[57-59]. Recently, Yang *et al.* conducted a systematic investigation into the impact of various atmospheres (water vapor, oxygen, carbon dioxide) on the degradation of Na layered oxides, using $\text{O}_3\text{-NaNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NFM111) as the model system^[60]. Researchers discovered that the XRD pattern maintained its original characteristics without any new peaks even after 48 h of individual exposure to water vapor, oxygen and carbon dioxide, or simultaneous exposure to oxygen and carbon dioxide for 48 h. However, peak shifts were observed in the presence of both water and oxygen. Further, in the combined presence of water and carbon dioxide, the formation of sodium bicarbonate occurred, highlighting water as a primary factor contributing to performance degradation [Figure 3A]. The rough surface and increased spacing of lattice fringes further prove the damaging effect of combined water vapor and CO_2 . The intercalation of CO_2 , CO_3^{2-} , H_3O^+ , or H_2O is ruled out by conducting Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) analyses and isotope-labeling strategies [Figure 3B]. Furthermore, powder neutron diffraction confirmed the integration of protons into tetrahedral sites within the sodium layers, potentially triggering acid degradation [Figure 3C]. Subsequent X-ray Absorption Spectroscopy (XAS) analysis demonstrated the oxidation of bulk Ni^{2+} by O_2 , a phenomenon that becomes more pronounced with higher Ni content, indicating the inadequate air stability of high-nickel materials [Figure 3D].

Owing to the larger radius of K^+ ions, the inferior air stability is notably pronounced in K layered oxides. $\text{P3-K}_{0.4}\text{Fe}_{0.1}\text{Mn}_{0.8}\text{Ti}_{0.1}\text{O}_2$ delivers a capacity of 115 mA h g^{-1} at 20 mA g^{-1} based on $\text{Fe}^{3+}/\text{Fe}^{4+}$ and $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox couple^[61]. However, significant capacity degradation was observed following a 7-day storage period in air, causing only 76 mA h g^{-1} to remain. XRD patterns reveal new diffraction peaks corresponding to K_2CO_3 and MnO phases [Figure 3E], which may originate from the K^+/H^+ exchange and disproportionation reaction of Mn^{3+} , respectively. The air instability of K layered oxides is a widely acknowledged issue. The XRD Rietveld refinement of $\text{P3-K}_{0.5}\text{Mn}_{0.7}\text{Fe}_{0.2}\text{Mg}_{0.05}\text{Cu}_{0.05}\text{O}_2$ (KMO) revealed the appearance of diffraction peaks, signaling the presence of H_2O and carbonate species after 14 days of exposure to air^[62]. And the surface of particles displayed increased imperfections post-exposure, adversely impacting ion transport kinetics. As depicted in Figure 3F, the discharge capacity of the exposed cathode (exp-KMO) only reached 46.1 mA h g^{-1} after 100 cycles at 0.5 C , representing 57.3% of the capacity exhibited by the fresh sample.

In short, the degradation process of the cathode in air can be divided into two stages [Figure 4]: (1) acid degradation. The layered oxides experience Na^+/H^+ ion exchange in air causing the removal of Na^+ ions and surface reduction of Mn^{4+} or Mn^{3+} , which results in significant cracking, curvature within interlayers, and surface reconstruction; (2) oxidative degradation. The transition metal ions are oxidized by water and oxygen, prompting the deintercalation of sodium ions and the formation of harmful residues on the surface, yielding the formation of a rock salt phase at the surface and a decrease in performance.

Interfacial instability

When an electrode interacts with an electrolyte, or throughout the procedures of charging and discharging, the formation of an electrode-electrolyte interphase (EEI) occurs on the electrode surfaces as a consequence

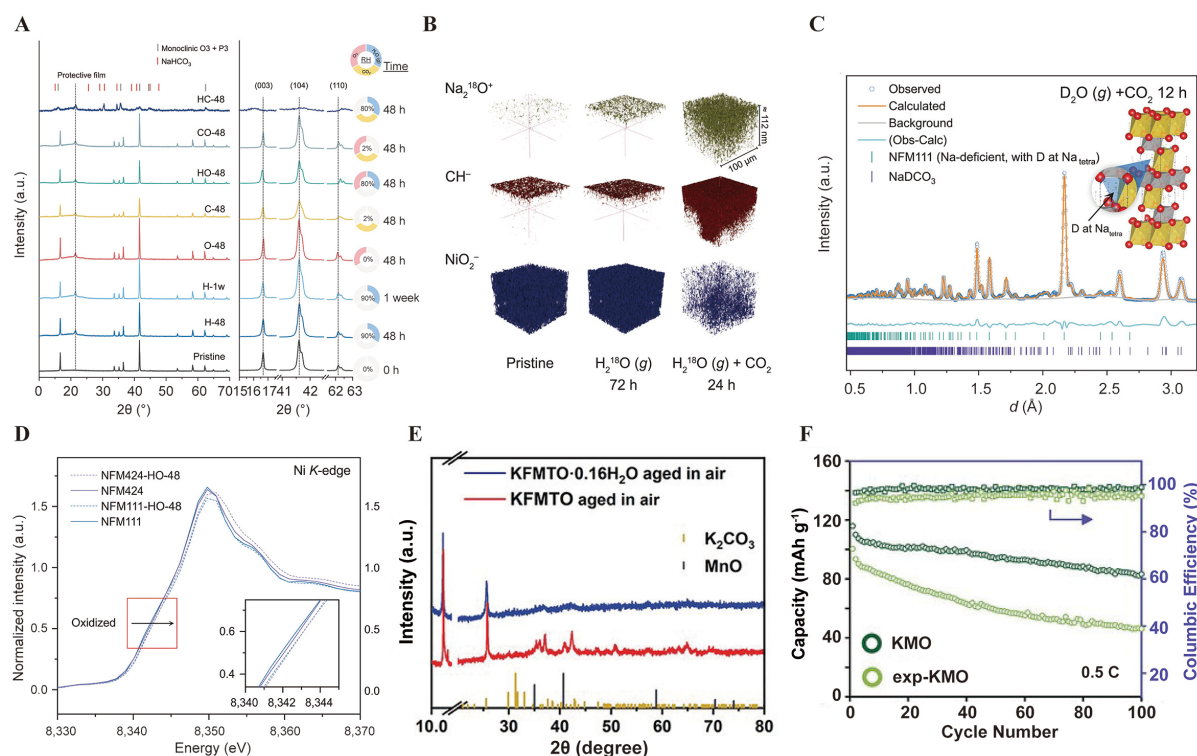


Figure 3. (A) XRD patterns of NFM111 exposed to different atmospheres with magnified regions of (003), (104), and (110)^[60]. (B) 3D rendering of selected representative secondary-ion fragments from ToF-SIMS characterization. Samples were stored in N₂ with H₂¹⁸O vapor for 72 h and in CO₂ with H₂¹⁸O vapor for 24 h^[60]. (C) Refinement of the NPD pattern of the sample stored in D₂O vapor and CO₂ for 12 h, where D atoms are placed at the tetrahedral sites in the Na layer (Na_{tetra} in inset)^[60]. (D) Ni K-edge XAS spectra of NFM111 and NFM424 before and after being stored in O₂ with water vapor (RH = 80%) for 48 h^[60]. (A–D) Figures reprinted with permission from Ref.^[60]. Copyright 2024 The American Association for the Advancement of Science^[60]. (E) The XRD patterns of KFMTO and KFMTO-0.16H₂O powder being aged in the air for seven days^[61]. Reprinted with permission from Ref.^[61]. Copyright 2022 Wiley-VCH^[61]. (F) cyclic performance of KMO and exp-KMO at 0.5 C^[62]. Reprinted with permission from Ref.^[62]. Copyright 2024 Wiley-VCH^[62].

of electrolyte reduction or oxidation, resulting from the thermodynamic equilibrium of energy levels between the electrodes and electrolyte [Figure 5A]^[63]. While the electrochemical potential of the cathode is below the highest occupied molecular orbital (HOMO) energy level of electrolyte, electrons transfer from the electrolyte to the cathode, causing electrolyte oxidation. In contrast, with the electrochemical potential of the anode surpassing the lowest unoccupied molecular orbital (LUMO) energy level of the electrolyte, electrons move from the negative electrode to the electrolyte, leading to electrolyte reduction. The EEI between the cathode and electrolyte is usually called a cathode electrolyte interphase (CEI). The interphase on the anode side is referred to as a solid electrolyte interphase (SEI)^[64,65].

The EEI typically acts as an ion conductor and electron insulator to ensure the stable cycling of batteries. On the cathode side, a robust and stable CEI is of critical importance in safeguarding the performance of the cathode material^[66,67]. Firstly, the occurrence of electron tunneling will continuously deplete the electrolyte if the cathode is not effectively passivated, leading to a decline in electrochemical performance. The CEI film formed on the surface of NFM111 in 1 M NaPF₆ in propylene carbonate (PC)/ethyl methyl carbonate (EMC) with 2% fluoroethylene carbonate (FEC) exhibits suboptimal thickness (1 nm), which is inadequate for efficient passivation of the electrode, accelerating the dissolution of transition metal ions^[68]. Secondly, the electrolyte, which contains PF₆⁻ ions or FEC, has the potential to generate HF during decomposition when subjected to high voltage^[69]. Additionally, the unequal distribution of electrons within the e_g orbitals of

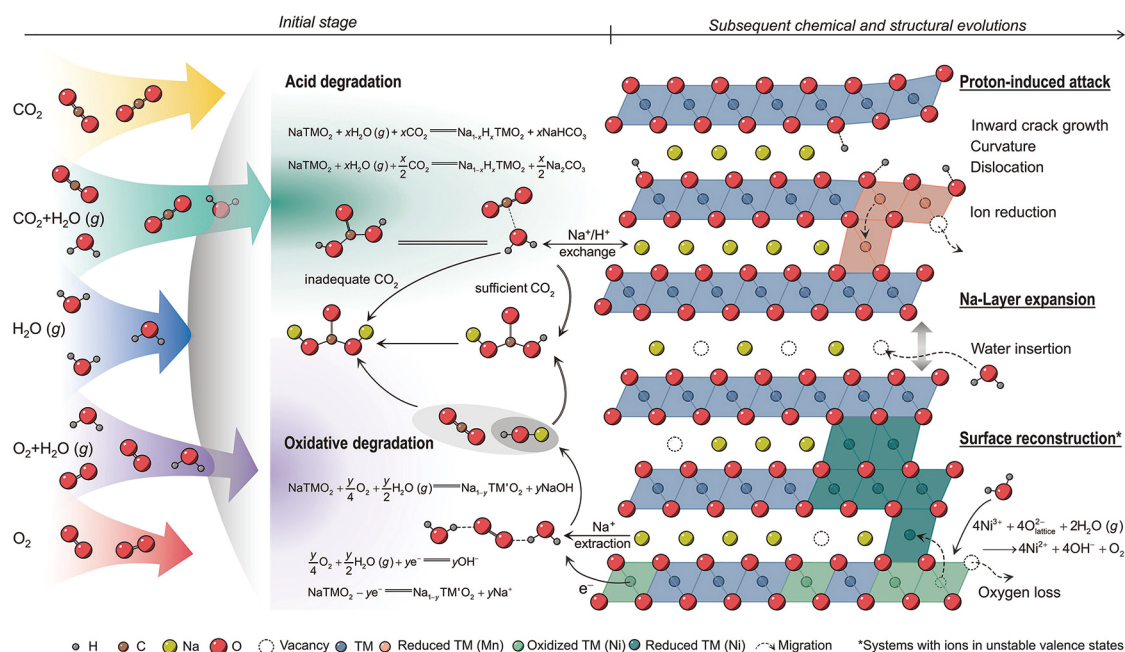


Figure 4. Illustration of degradation mechanisms for O3-NLOs in the air^[60]. Reprinted with permission from Ref.^[60]. Copyright 2024 The American Association for the Advancement of Science^[60].

Jahn-Teller effect ions (e.g., Mn^{3+} , Cu^{2+} , Fe^{4+}) may result in varying degrees of stretching or compression in the TM-O bonds of the TMO_6 octahedra [Figure 5B]. It has been demonstrated that oxygen atoms on elongated TM-O bonds possess a more negative charge, rendering them susceptible to reacting with HF. Consequently, transition metal ions may subsequently dissolve into the electrolyte, causing structural collapse [Figure 5C]^[70]. The X-ray Photoelectron Spectroscopy (XPS) spectra on post-cycled separators further confirmed the dissolution of iron and manganese [Figure 5D]^[71]. The results from electron energy loss spectroscopy (EELS) of $\text{O}_3\text{-Na}_{1/3}\text{Ni}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_2$ illustrate a low-to-high energy shift in the Mn L-edge from the surface to the bulk and an increasing intensity of the O K-edge which imply surface reduction of Mn and oxygen loss [Figure 5E]. Furthermore, the surface reconstruction, nano-cracks and dislocations arise from the side reactions between the electrode and electrolyte, diminishing the kinetic performance and reducing the cycling lifespan.

During the discharging process, the valence state of Mn undergoes a change from Mn^{4+} to Mn^{3+} , which is followed by disproportionation reactions that transform Mn^{3+} into Mn^{2+} and Mn^{4+} . Subsequently, the Mn^{2+} is dissolved into the electrolyte^[22,72]. $\text{P3-K}_{0.5}\text{MnO}_2$ shows a notable specific capacity above 110 mA h g^{-1} at 20 mA g^{-1} , but exhibits a poor cycling performance with only 20% of the capacity retained after 300 cycles^[73]. A high content of Mn was detected on the post-cycling separator, indicating severe transition metal dissolution, which ultimately resulted in a reduction in cycle life. Similarly, P2-type $\text{K}_{0.5}\text{Ni}_{0.1}\text{Mn}_{0.9}\text{O}_2$ (KNMO) exhibits four distinct redox pairs, with the pairs exceeding 2.8 V corresponding to $\text{Ni}^{2+}/\text{Ni}^{3+}$ and $\text{Ni}^{3+}/\text{Ni}^{4+}$ and the other relates to $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox processes [Figure 5F]^[74]. Nevertheless, a notable shift in Cyclic Voltammetry (CV) peaks is displayed by KNMO due to unwanted side reactions and electrochemical polarization. A SEM image demonstrates the existence of significant particle microfractures in unprocessed KNMO particles, originating from tensile stresses induced by prolonged cycling-induced anisotropic lattice contraction/expansion [Figure 5G]. These microcracks facilitate enhanced electrolyte permeation and expose the internal surface to electrolyte aggression, thereby causing persistent capacity degradation and

leading to structural collapse.

STRATEGIES

As previously discussed, the bulk properties and interface characteristics of the cathode profoundly influence electrochemical performance. These attributes are primarily governed by three key factors: the composition of the cathode, the distribution of elements within the cathode, and the compatibility between the electrode and electrolyte. With this respect, numerous optimization strategies, such as element doping, surface modification, structure design and electrolyte optimization, have been demonstrated to significantly enhance electrode performance. Consequently, a detailed discussion of these strategies will be provided.

Element doping

K_xMnO_2 , benefiting from the low cost of Mn resources and its outstanding capacity, has become a widely utilized K layered oxide cathode. However, the insufficient structural reversibility under high-voltage operation and transition metal dissolution during cycling have a detrimental impact on its performance^[75-78]. It is recognized that the composition of the cathode is a key factor in determining the effect of the electrode. With the appropriate substitution of elements, the intrinsic crystal structure and ion state can be substantially modulated which can help to improve stability and suppress structure collapse.

Suppressing irreversible phase transition

The K_xMnO_2 cathode exhibits a complex structural transition during the charging and discharging process, resulting in a significant volume change and rapid capacity loss. To inhibit the P3-O3 phase transition and Jahn-Teller effect of Mn^{3+} , the doping/substitution of the cathode with electrochemically active elements (Ni, Fe, Co, Cu, *etc.*) or inactive elements (Mg, Ti, Al, Zn, *etc.*) has been widely investigated.

Doping electrochemically active elements can both stabilize the structure and boost the capacity. Ni-substituted $P2-K_{0.44}Ni_{0.22}Mn_{0.78}O_2$ delivers a first discharge capacity of 125.5 mA h g⁻¹ at 10 mA g⁻¹ with a capacity retention of 67% after 500 cycles at 200 mA g⁻¹ between 1.5-4 V based on Ni^{2+}/Ni^{3+} , Ni^{3+}/Ni^{4+} and Mn^{3+}/Mn^{4+} redox couple [Figure 6A]^[41]. Results from *in-situ* XRD found that there are no impurity peaks throughout the charging/discharging process indicating a single solid-solution reaction with small volume change of 1.5%. Besides nickel^[42,79], other elements such as iron^[80,81], nickel and cobalt^[82-85] are also effective substitution elements to improve cycling life and electrical conductivity. $P3-K_{0.5}Mn_{0.8}Fe_{0.1}Ni_{0.1}O_2$ exhibits a high specific capacity, coupled with a P3-O3 phase transition when charging from 3.5 to 3.9 V^[79]. However, the O3-X phase transition observed in $K_{0.5}MnO_2$ disappears, which is attributed to the substitution of Mn^{3+} site by Fe^{3+} and Ni^{2+} suppressing the additional phase transition [Figure 7A]. *In-situ* XRD patterns of the $P3-K_xCo_{0.5}Mn_{0.5}O_2$ and DFT calculation confirmed a single-phase reaction during K^+ extraction and insertion^[82]. In the pristine $P3-K_{0.75}MnO_2$, two Mn-O bonds have longer stretches than the other bonds within the MnO_6 octahedra. Conversely, all of the Mn-O bonds within the MnO_6 octahedra exhibit similar lengths in the Co-substituted $P3-K_{0.75}Co_{0.5}Mn_{0.5}O_2$, indicating the effectiveness of Co-substitution in alleviating the Jahn-Teller distortion caused by Mn^{3+} in the cathode [Figure 7B]. Nevertheless, the widespread application of cobalt-containing layered oxides is constrained by the toxicity and high cost associated with cobalt^[83].

As electrochemically inactive ions do not engage in redox reactions, more K^+ ions are maintained within the alkali metal layer, thus partially restraining the gilding of transition metal layers^[86-89]. Huang *et al.* prepared a $P3-K_{0.54}Mn_{0.78}Mg_{0.22}O_2$ cathode, which exhibits a superior specific capacity of 132.4 mA h g⁻¹ at 20 mA g⁻¹ from 1.5 to 4.0 V on the basis of Mn^{3+}/Mn^{4+} redox couple [Figure 6B]^[90]. The widened oxidation-reduction peaks and smooth galvanostatic charge-discharge (GCD) curves imply that Mg substitution reduces the

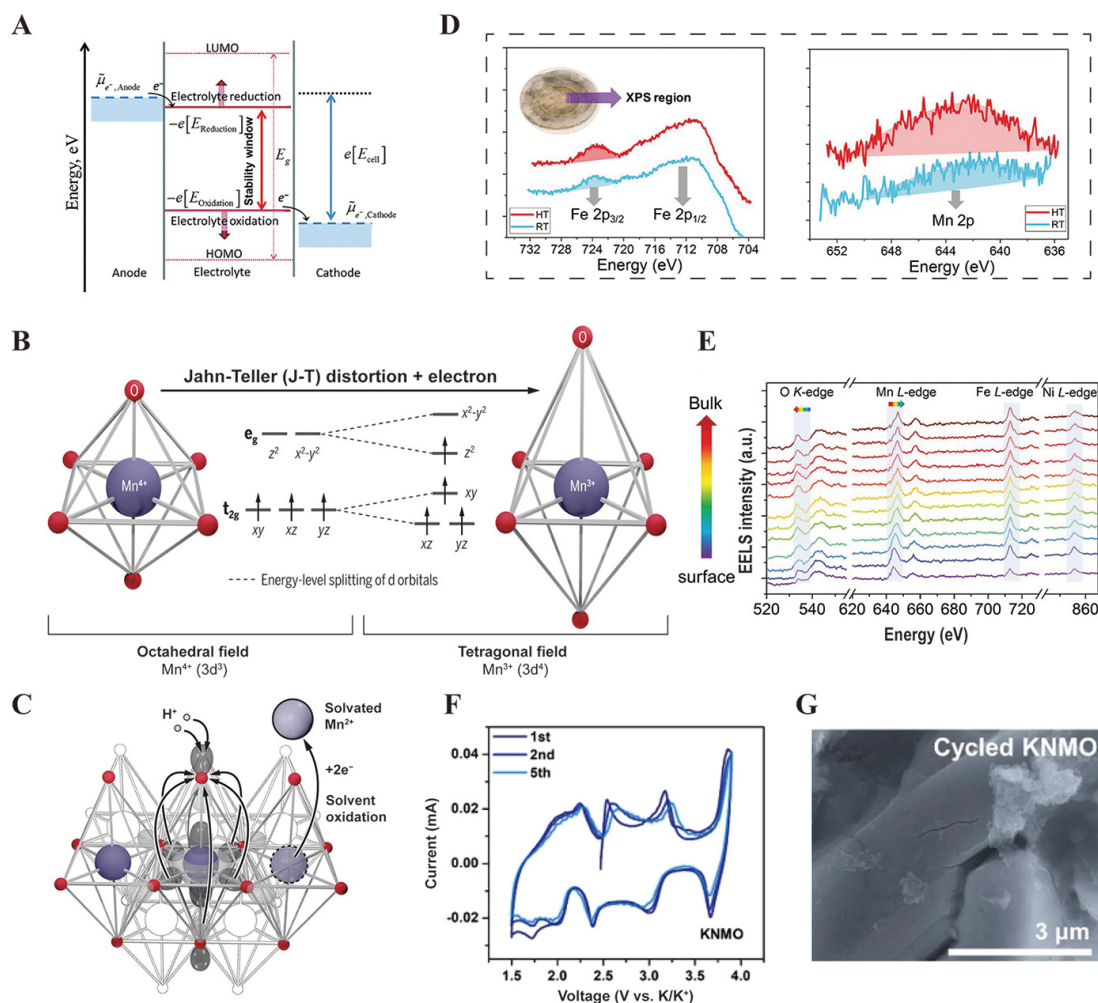


Figure 5. (A) Schematic illustrating the energy states of the electrodes and the electrolyte, leading to the formation of the SEI and cathode electrolyte interphase^[63]. Reprinted with permission from Ref.^[63]. Copyright 2020 Royal Society of Chemistry^[63]. (B) The ligand field in manganese oxides and the schematic diagram of the J-T distortion of Mn^{3+} ^[70]. (C) Diagram of transition metal ion dissolution^[70]. (B and C) Figures reprinted with permission from Ref.^[70]. Copyright 2020 The American Association for the Advancement of Science^[70]. (D) The Fe 2p and Mn 2p spectra from the light-yellow region of the separator after being cycled in cells 20 times at 25 and 45 °C^[71]. (E) EELS spectra of O K-edge, Mn, Co and Ni L-edges collected from the surface to the subsurface on a representative particle with an increment of 1 nm per spectrum^[71]. (D and E) Figures reprinted with permission from Ref.^[71]. Copyright 2018 Wiley-VCH^[71]. (F) CV curves at the scan rate of 0.1 mV s⁻¹ for KNMO in the initial five cycles^[74]. (G) SEM image of the cycled electrodes^[74]. (F and G) Figures reprinted with permission from Ref.^[74]. Copyright 2023 Wiley-VCH^[74].

irreversible transformation and bolsters structural stability. Considering that both Mn^{4+} and Ti^{4+} share an identical valence state and have a comparable ionic radius (0.605 Å of Ti^{4+} vs. 0.53 Å of Mn^{4+}). A series of $P2-K_{5/9}Mn_{1-x}Ti_xO_2$ ($x = 0, 1/9, 2/9, 3/9$ and $4/9$) (designed as KMTO-x) was fabricated via solid-state reaction method^[91]. Although the specific capacity decreases slightly with an increase in Ti content, a smooth voltage profile was achieved which can be attributed to the suppressed phase transition [Figure 6C]. Further, *in-situ* XRD patterns of KMTO-0 and KMTO-2/9 between 1.5 and 4.2 V showed that the detrimental P2-O2 phase transition in KMTO-0 was diminished, giving rise to a stable OP4 phase in KMTO-2/9 charging to 4.2 V which exhibited significantly higher reversibility in comparison to the P2-O2 phase transition [Figure 7C]. It is noteworthy that while the doping of Mg^{2+} and Ti^{4+} can inhibit phase transitions to some extent, research has revealed that the valence state of Mn sometimes holds a primary effect in ensuring the integrity of the layered oxides^[92]. The Mn valence of $K_{0.5}Mn_{0.7}Co_{0.2}Fe_{0.1}O_2$ (KMCFO), $K_{0.5}Mn_{0.6}Co_{0.2}Fe_{0.1}Ti_{0.1}O_2$ (KMCFTO)

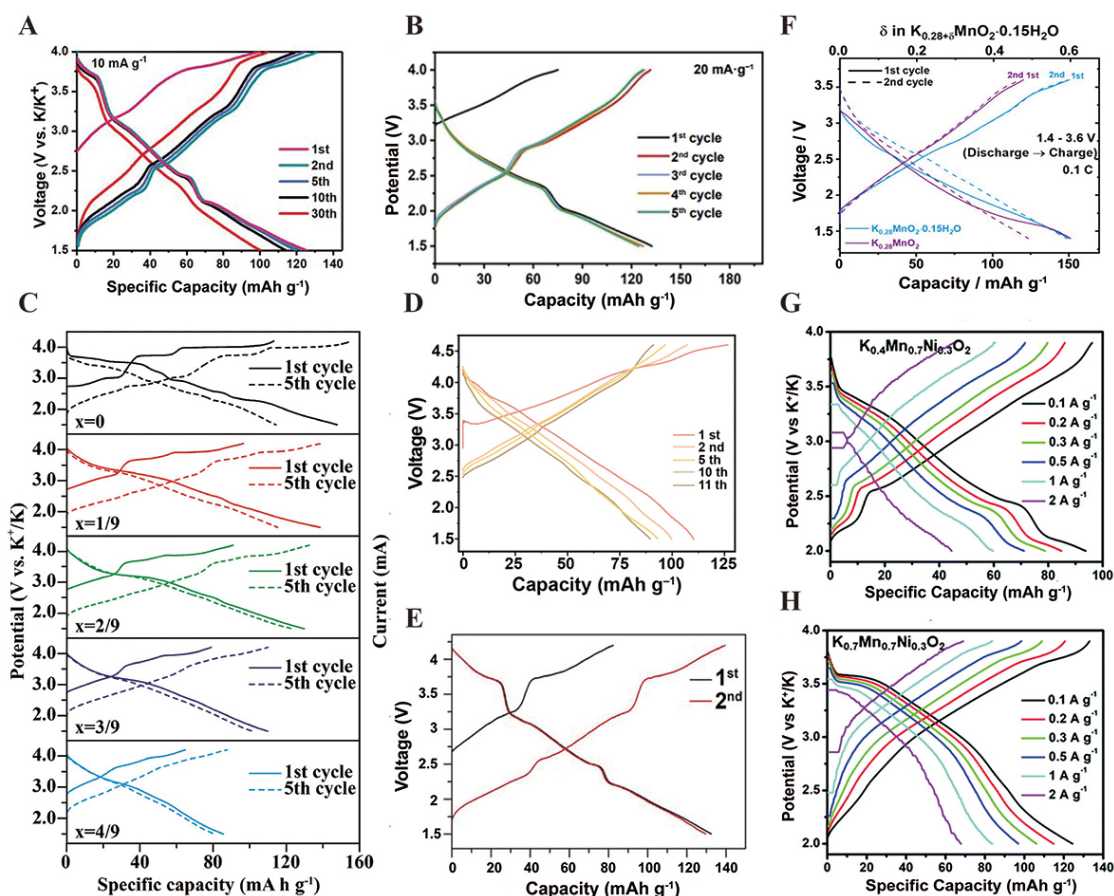


Figure 6. GCD curves of (A) P2- $\text{K}_{0.44}\text{Ni}_{0.22}\text{Mn}_{0.78}\text{O}_2$ [41]. Reprinted with permission from Ref. [41]. Copyright 2019 Wiley-VCH [41]. (B) $\text{K}_{0.54}\text{Mn}_{0.78}\text{Mg}_{0.22}\text{O}_2$ [90]. Reprinted with permission from Ref. [90]. Copyright 2021 Springer Nature [90]. (C) KMTO- x [91]. Reprinted with permission from Ref. [91]. Copyright 2020 Elsevier [91]. (D) P2- $\text{K}_{0.56}\text{Na}_{0.11}\text{Li}_{0.12}\text{Ni}_{0.22}\text{Mn}_{0.66}\text{O}_2$ [46]. Reprinted with permission from Ref. [46]. Copyright 2024 Royal Society of Chemistry [46]. (E) P2- $\text{K}_{2/3}\text{Mn}_{7/9}\text{Ni}_{1/9}\text{Ti}_{1/9}\text{O}_{17/9}\text{F}_{1/9}$ [97]. Reprinted with permission from Ref. [97]. Copyright 2022 American Chemical Society [97]. (F) $\text{K}_{0.28}\text{MnO}_2 \cdot 0.15\text{H}_2\text{O}$ [100]. Reprinted with permission from Ref. [100]. Copyright 2019 American Chemical Society [100]. (G) $\text{K}_{0.4}\text{Mn}_{0.7}\text{Ni}_{0.3}\text{O}_2$ [43]. (H) $\text{K}_{0.7}\text{Mn}_{0.7}\text{Ni}_{0.3}\text{O}_2$ [43]. (G and H) Figures reprinted with permission from Ref. [43]. Copyright 2020 Royal Society of Chemistry [43].

and $\text{K}_{0.5}\text{Mn}_{0.6}\text{Co}_{0.2}\text{Fe}_{0.1}\text{Mg}_{0.1}\text{O}_2$ (KMCFO) is +3.714, +3.667 and +4, respectively. *In-situ* XRD demonstrates the KMCFO and KMCFTO undergo P3-O3 phase transition when charging from 3.4 V to discharging at 3.0 V [Figure 7D]. Although the doping of Ti^{4+} was expected to inhibit the phase transition, this effect was nullified by the reduction in the Mn valence. On the contrary, the Mg-doped material with a Mn valence of +4 exhibits a solid solution reaction during de/potassiation. The split high energy e_g orbitals calculated by DFT also indicate the existence of Jahn-Teller active Mn^{3+} ions, which degrade the cathode stability.

The implementation of light-weight ions (such as Li^+ [46,93,94], F^- [95-97] and B^{3+} [98,99]) within the transition metal layer facilitates the reinforcement of covalent bonds with adjacent O atoms and adjusts the redox behavior. P2- $\text{K}_{0.56}\text{Na}_{0.11}\text{Li}_{0.12}\text{Ni}_{0.22}\text{Mn}_{0.66}\text{O}_2$ obtained by electrochemical ion exchange exhibits a high reversible capacity and excellent structural stability at high voltage with a single solution reaction during the charging-discharging process [Figure 6D] [46]. The Li-doped material displays a more even and continuous GCD curve than the pure sample, indicating the K^+ /vacancy ordering has been effectively mitigated. The F-doped P2- $\text{K}_{2/3}\text{Mn}_{7/9}\text{Ni}_{1/9}\text{Ti}_{1/9}\text{O}_{17/9}\text{F}_{1/9}$ cathode not only delivers a substantial capacity of $132.5 \text{ mA h g}^{-1}$ within 1.5-4.2 V [Figure 6E] but also exhibits a good cycling performance, retaining 91% of its capacity after 50 cycles at

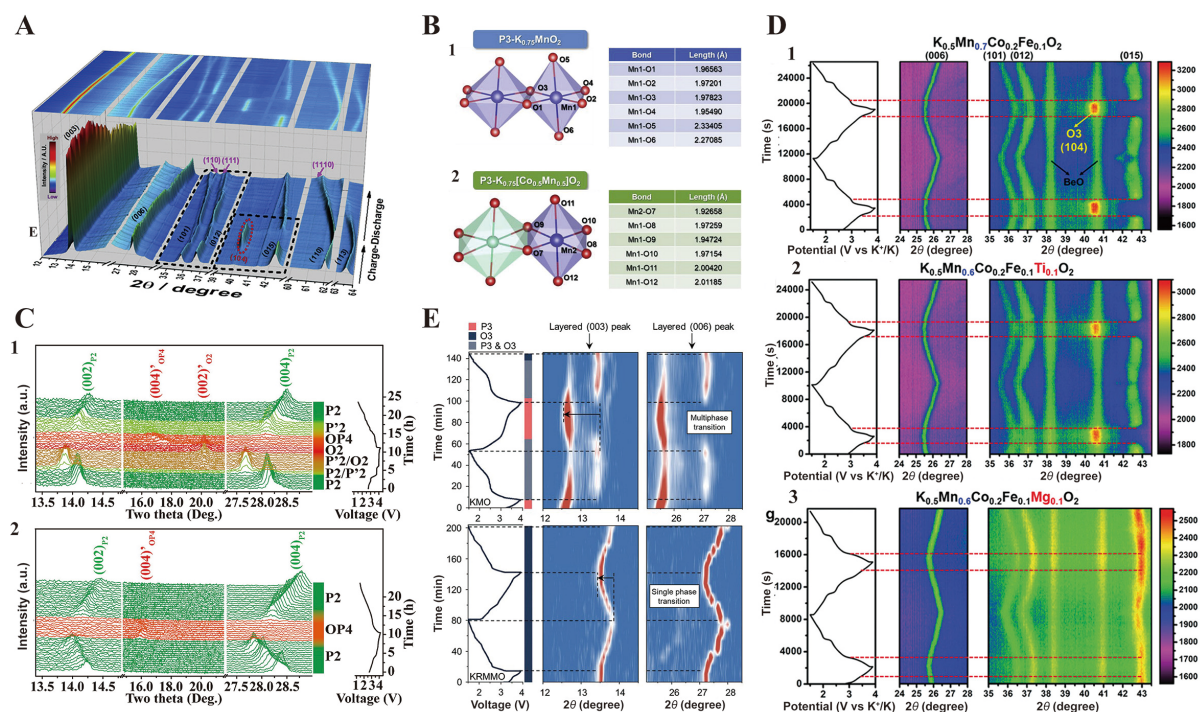


Figure 7. *In-situ* XRD patterns of (A) P3-K_{0.5}Mn_{0.8}Fe_{0.1}Ni_{0.1}O₂ [79]. Reprinted with permission from Ref [79]. Copyright 2020 Elsevier [79]. Mn-O bonding distances of (B1) P3-K_{0.75}MnO₂ [82] and (B2) P3-K_{0.75}Co_{0.5}Mn_{0.5}O₂ [82]. Reprinted with permission from Ref. [82]. Copyright 2019 Elsevier [82]. *In-situ* XRD patterns of (C1) P2 KMTO-O [91], (C2) P2 KMTO-2/9 [91]. Reprinted with permission from Ref. [91]. Copyright 2020 Elsevier [91]. *In-situ* XRD characterization of (D1) K_{0.5}Mn_{0.7}Co_{0.2}Fe_{0.1}O₂ [92], (D2) K_{0.5}Mn_{0.6}Co_{0.2}Fe_{0.1}Ti_{0.1}O₂ [92], and (D3) K_{0.5}Mn_{0.6}Co_{0.2}Fe_{0.1}Mg_{0.1}O₂ [92]. Reprinted with permission from Ref. [92]. Copyright 2021 Wiley-VCH [92]. (E) *In-situ* XRD patterns of K_{0.5}MnO₂ and KRMMO [104]. Reprinted with permission from Ref. [104]. Copyright 2022 Wiley-VCH [104].

100 mA g⁻¹, accompanying with a solid solution reaction [97]. Besides, the DFT results demonstrate that F⁻ anions promote electronic conductivity. P3-K_{0.5}Mn_{0.8}Co_{0.2}B_{0.1}O₂ (KMCBO) was synthesized using a solid-state method, with boron inserted into an interstitial tetrahedral site [98]. The *in-situ* XRD results reveal that a P3-O3 phase transition, which exists in P3-K_{0.5}MnO₂ with K⁺ ion extraction, was suppressed. Moreover, a noticeable reduction in the Mn *e_g* energy is detected post-boron incorporation, indicated by the movement of the Density of States (DOS) peak towards the Fermi level. This shift extends into a portion of the Mn *t_{2g}* orbital, enhancing the charge transfer speed.

In addition to substituting atoms within the transition metal layers, the introduction of inactive elements into the alkali metal layers to serve as interlayer pillars has been noted to impede the slippage of transition metal layers, consequently inhibiting phase transition [100–104]. Jo *et al.* have obtained K_{0.28}MnO₂·0.15H₂O, which shows a capacity of 150 mA h g⁻¹ at 15 mA g⁻¹ and with 81% capacity retention over 100 cycles compared with 38% for K_{0.28}MnO₂ [Figure 6F] [100]. The operando XRD results show that no notable impurity peaks appear in the host structure during de/potassiation and water molecules remaining in the K layer play an important role as a pillar to support the structure. Apart from introducing crystalline water between layers, certain metal ions can also suppress the gliding of transition metal layers. In comparison to P3-K_{0.5}MnO₂, the decline in capacity of P3-K_{0.45}Rb_{0.05}Mn_{0.85}Mg_{0.15}O₂ (KRMMO) is notably mitigated, primarily due to the synergistic effect of Rb and Mg ions in the alleviation of volume change and inhibition of phase transition [104]. The combined stabilizing impact of Rb and Mg substitution facilitated the suppression of transition metal layers sliding, the transformation from O3-type to P3-type and improved the structural stability of KRMMO [Figure 7E]. However, the introduction of inactive particles into the

alkali metal layer may affect the diffusion of K^+ leading to deteriorated kinetic performance and reduced capacity.

A high-entropy strategy with five or even more metal elements has been widely used in SIBs^[105]. Electrochemical performance and material stability can be enhanced through the synergistic effects of multiple elements^[106–110]. The ordering structure usually increases the diffusion barrier for K^+ ions, thus inhibiting the diffusion dynamics. Conversely, the introduction of disorder not only facilitates the ion diffusion, improving the rate performance, but also generates additional storage sites for K^+ ions. Analysis of Selected Area Electron Diffraction (SAED) patterns for $K_{0.7}Fe_{0.05}Co_{0.1}Mn_{0.75}Ni_{0.05}V_{0.05}O_2$ (KFCMNV) revealed no evidence of superlattice reflections along the $[-111]$ zone axis, in contrast to the ordered P3-KFCMN and P3-KFCMV^[106]. The difference in redox couple potentials between P3-KFCMN and P3-KFCMV (0.413 and 0.526 V) was greater than that observed in P3-KFCMNV (0.386 V), indicating that the cathode with TM disordering exhibits commendable redox reversibility and superior rate performance. Besides inhibiting K^+ /vacancy ordering through element doping, Xiao *et al.* discovered that a K^+ /vacancy disordered structure can also be constructed by adjusting the potassium content^[43]. Compared with $K_{0.4}Mn_{0.7}Ni_{0.3}O_2$, the superlattice spots are not visible in $K_{0.7}Mn_{0.7}Ni_{0.3}O_2$ through the SAED pattern. And the smoother GCD curves and CV curves additionally suggest a transition in the cathode structure from K^+ /vacancy ordering to K^+ /vacancy disordering with increasing potassium content [Figure 6G and H].

Enhancing air stability and interface stability

The aforementioned substituted elements primarily target the suppression of phase transitions and enhancement of structural stability. Additionally, certain metal ions show a positive impact on enhancing both air stability and interface stability^[96,98,111,112]. Cu^{2+} has been shown to exhibit electrochemical activity in layered transition metal oxides for SIBs and can also enhance the air stability of layered cathodes effectively^[113]. Park *et al.* combined machine learning and DFT calculations to design a P'3- $K_{0.3}Mn_{0.9}Cu_{0.1}O_2$ (KMCO) cathode^[111]. The similar Mn-O band length in KMCO suggests a suppression of Jahn-Teller distortion. Significantly, analysis of the *ex-situ* XPS and *ex-situ* X-ray absorption near edge structure (XANES) spectra revealed a Cu^{2+}/Cu^{3+} redox activity centered around 3.4 V, implying the electrochemical activity of Cu^{2+} in PIBs [Figure 8A]. Furthermore, the XRD patterns of KCMO displayed no discernible variance between the pristine samples and those exposed to air for four weeks, indicating a substantial enhancement in air stability associated with Cu^{2+} doping. In contrast, the presence of the hydrate phase and K_2CO_3 phase was evident in $K_{0.3}MnO_2$ following exposure to air [Figure 8B and C]. Al-doped $K_{0.45}Mn_{0.9}Al_{0.1}O_2$ exhibits an outstanding capacity (152 mA h g^{-1} at 20 mA g^{-1}) and a remarkable long cycling performance (67% for Al-doped material *vs.* 44% for pure sample over 1,000 cycles at 500 mA g^{-1})^[112]. The High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy (HAADF-STEM) image reveals a reduction in dislocations and twin boundaries within Al-doped $K_{0.45}MnO_2$, establishing a smooth K^+ ion transport channel [Figure 8D]. The High-Resolution Transmission Electron Microscopy (HRTEM) images illustrate that a thin and uniform CEI was fabricated in the Al-doped cathode, while the AlF_3 protection layer effectively mitigates Mn dissolution, contributing to the substantially enhanced cycle stability [Figure 8E]. Apart from Al, dopant elements such as F and B have been discovered to participate in the formation of interfacial phases, establishing interphases rich in inorganic components to effectively passivate the cathode surface and suppress the dissolution of metal ions^[96,98]. The interlayer water molecule not only stabilizes structure, as mentioned previously, but also enhances air stability for some cathodes. The hydrated $K_{0.4}Fe_{0.1}Mn_{0.8}Ti_{0.1}O_2 \cdot 0.16H_2O$ (KFMT0-0.16 H_2O) was prepared by immersing and stirring $K_{0.4}Fe_{0.1}Mn_{0.8}Ti_{0.1}O_2$ (KFMT0) powders in distilled water for 10 h^[61]. The XRD pattern of KFMT0-0.16 H_2O after a 60-day period of exposure has no impurity [Figure 8F], ascribed to the water molecule which inhibited K^+/H^+ ion exchange and the extraction of K^+ upon exposure to air. At a current density of

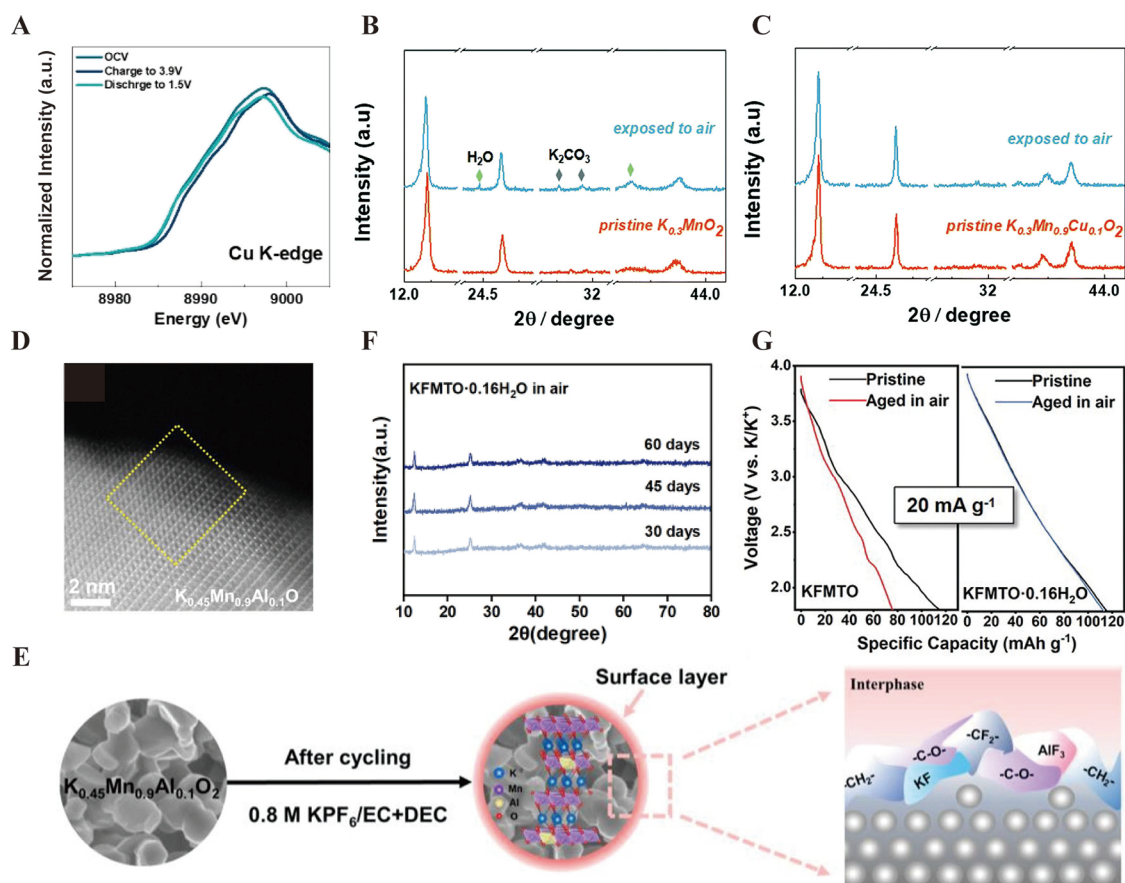


Figure 8. (A) Cu K-edge ex-situ XANES spectra of KMCO^[111]. Comparison of XRD patterns of (B) $K_{0.3}MnO_2$ and (C) KMCO between pristine and after four-week air exposure^[111]. (A-C) Figures reprinted with permission from Ref.^[111]. Copyright 2021 Royal Society of Chemistry^[111]. (D) HAADF-STEM image of $K_{0.45}Mn_{0.9}Al_{0.1}O_2$ along the [100] zone axes^[112]. (E) Schematic illustration of the interphase layer for $K_{0.45}Mn_{0.9}Al_{0.1}O_2$ electrode after cycling^[112]. (D and E) Figures reprinted with permission from Ref.^[112]. Copyright 2023 Elsevier. (F) The XRD patterns of KFMT0 and KFMT0-0.16H₂O powder being aged in the air for seven days^[61]. (G) GCD curves of the pristine and aged KFMT0 and KFMT0-0.16H₂O^[61]. (F and G) Figures reprinted with permission from Ref.^[61]. Copyright 2022 Wiley-VCH^[61].

20 mA g⁻¹, the GCD profiles of the aged KFMT0-0.16H₂O electrode showed nearly no capacity loss compared to the initial sample, whereas the aged KFMT0 electrode experienced considerable capacity loss [Figure 8G].

Surface modification

Surface modification is an efficient way to prevent the dramatic volume variation^[74,114,115], side reaction between cathode and electrolyte^[62,116,117] and dissolution of metal ions during charging and discharging^[73,118,119]. The common coating layers mainly include oxides, phosphates, fluorides and organic compounds. In comparison to the pristine $K_{0.5}MnO_2$, the Al_2O_3 -modified P3- $K_{0.5}MnO_2$ ($K_{0.5}MnO_2@Al_2O_3$) achieves a CE exceeding 95%, while the original cathode demonstrates a CE of only 87% after 300 cycles. This enhancement can be ascribed to the effective reduction of side reactions on the interface by the coating layer^[73]. Analysis of the electrochemical impedance spectroscopy (EIS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) results reveals that the $K_{0.5}MnO_2@Al_2O_3$ electrode exhibits significantly lower R_{SEI} and R_{ct} [Figure 9A], along with decreased levels of dissolved Mn, when contrasted with the $K_{0.5}MnO_2$ electrode, suggesting that coating layer enhances charge transfer efficiency and alleviates structural degradation.

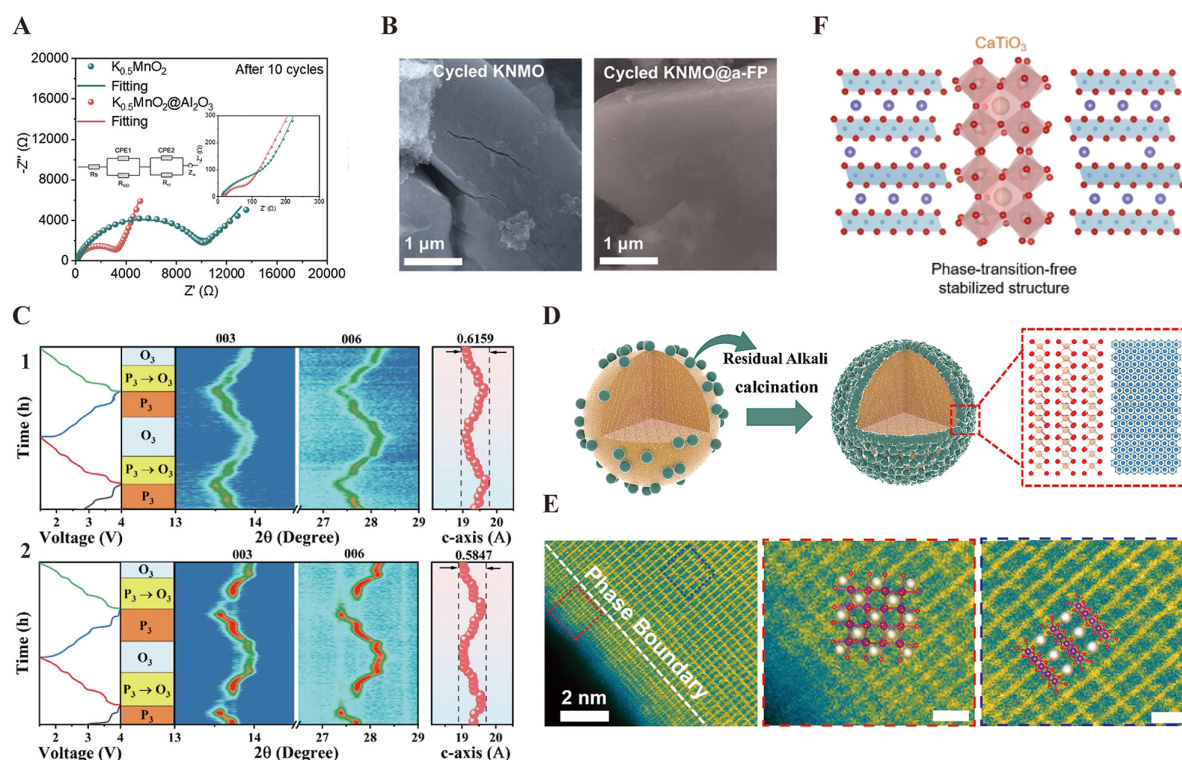


Figure 9. (A) Nyquist plots with the insets of high-frequency semicircles and corresponding equivalent circuits of $K_{0.5}MnO_2$ and $K_{0.5}MnO_2@Al_2O_3$ after 10 cycles^[73]. Reprinted with permission from Ref.^[73]. Copyright 2023 Elsevier.^[73] (B) SEM images of the cycled electrodes^[74]. Reprinted with permission from Ref.^[74]. Copyright 2023 Wiley-VCH^[74]. (C) In-situ XRD spectra of (C1) KMCF and (C2) KMCF- $P_{0.1}$ ^[118]. Reprinted with permission from Ref.^[118]. Copyright 2024 Elsevier^[118]. (D) the schematic diagram of the KMTO structure^[119]. Reprinted with permission from Ref.^[119]. Copyright 2024 Elsevier^[119]. (E) HADDF-STEM image of W-KMFMCO, indicative of the phase boundary. Reprinted with permission from Ref.^[62]. Copyright 2024 Wiley-VCH^[62]. (F) The schematic illustration of phase-transition-free $CaTiO_3$ stabilized KMT^[115]. Reprinted with permission from Ref.^[115]. Copyright 2024 Springer Nature^[115].

A flexible coating layer is often considered to better mitigate the stress generated by volume variations, thereby minimizing the development of surface cracks. In terms of cycling performance, KNMO modified with amorphous $FePO_4$ (KNMO@a-FP) demonstrates superior stability (66% capacity retention after 2,500 cycles) compared to the pristine KNMO and crystalline $FePO_4$ coated KNMO (KNMO@c-FP)^[74]. The SEM images of the cycled cathode also show that cracks on the particle surfaces are eliminated in KNMO@a-FP, which can be attributed to the effective release of lattice stress by the elastic layer [Figure 9B]. Additionally, the KNMO@a-FP was found to deliver a larger capacity controlled by pseudocapacitance, exhibiting a rapid diffusion of K^+ ions. Similarly, severe intragranular cracks and surface reconstruction are observed in P_3 - $K_{0.5}Mn_{0.8}Co_{0.2}O_2$ (KMCO) after being cycled for 50 cycles. EELS findings proved the pure sample has more O loss and Mn ions dissolution that severely degrades the cathode. On the contrary, fewer cracks and voids are formed on the KMCO particles modified with amorphous K_3PO_4 and crystalline $MnPO_4$ (P-KMCO). The pouch cell of P-KMCO||K@CC exhibits commendable electrochemical performance, delivering a high capacity of 110 mA h g^{-1} at 100 mA g^{-1} and a good capacity retention of 81.7% after 100 cycles^[114].

Surface modification can not only suppress interfacial side reactions and alleviate mechanical stress but also achieve the reversible phase transition of the cathode. Two types of $K_{0.5}Mn_{0.85}Co_{0.1}Fe_{0.05}O_2$ (KMCF) cathodes coated with $KMn_4(PO_4)_3$ were obtained through quenching technology, designated as KMCF- $P_{0.1}$ and KMCF- $P_{0.3}$, where the numbers 0.1 and 0.3, respectively, represent the concentrations of $NH_4H_2PO_4$

solutions used^[118]. Compared with KMCF and KMCF- $P_{0.3}$, a better cycling stability was achieved in KMCF- $P_{0.1}$ whose capacity retained 67.75 mA h g⁻¹ even after cycling 500 cycles at 2 C. In the *in-situ* XRD spectra, it is found while both KMCF and KMCF- $P_{0.1}$ experienced comparable phase transition processes, the main peak of KMCF decreases in intensity during the second charge-discharge cycle. Conversely, the high reversibility was maintained in KMCF- $P_{0.1}$ propelling stable long cycles [Figure 9C]. Surface residual alkali usually exhibits low conductivity, leading to decreased electrochemical performance and compromising air stability of the cathode. Meanwhile, the PVDF can be deactivated by residual alkali, rendering the preparation of the electrode more challenging. Shi *et al.* developed a method to convert surface residual alkali into a $KTaO_3$ coating layer [Figure 9D], significantly enhancing the cycling stability and air stability of the cathode, while inhibiting the dissolution of transition metal ions^[119]. Further, due to the unique ion diffusion path, the kinetic performance was also improved.

Upon exposure to air, layered potassium oxides frequently undergo structural degradation and surface reconstruction as a result of water molecule insertion and K^+/H^+ ion exchange, significantly affecting electrochemical performance. Constructing a physical barrier on the cathode to block direct contact with air can effectively improve the air stability of the cathode. Cai *et al.* effectively improved the air stability of $K_{0.6}Ni_{0.2}Co_{0.3}Mn_{0.5}O_2$ cathode through surface treatment using the plasma-enhanced sintering technique^[120]. In terms of surface quality, the bare cathode synthesized via the solid-state method (T-KNCMO) exhibits a comparatively more contaminated surface. In contrast, a noticeably cleaner surface was found on the modified cathode (PE-KNCMO). Even after being placed in the air for 30 days, PE-KNCMO maintained a capacity nearly equivalent to its initial state, showing a significant improvement in air stability. Recently, Liu *et al.* achieved a significant enhancement in the air stability of the cathode by immersing the layered $K_{0.5}Mn_{0.7}Fe_{0.2}Mg_{0.05}Cu_{0.05}O_2$ cathode in water (W-KMFMCO) and successfully constructing a potassium-rich spinel phase on its surface [Figure 9E]^[62]. XRD analysis reveals that the cathode can maintain its original structure even after being exposed to air for 14 days, with the capacity and cycle life remaining nearly unchanged. Compared to the layered phase, the spinel phase exhibits lower H_2O/CO_2 molecule adsorption energy, which is beneficial for enhancing air stability. Combining doping and coating can improve material performance from bulk to surface. Chen *et al.* synthesized $K_{0.5}Mn_{0.9}Ti_{0.1}O_2@CaTiO_3$ ^[115]. $CaTiO_3$ can be regarded as a clamp to prevent the transition metal layer from shifting and twisting throughout the charge and discharge cycles. And the Ti^{4+} partially replaced Mn^{3+} in the transition metal layer, reducing the Jahn-Teller effect and impeding the phase transition [Figure 9F]. The modified cathode achieves 119.3 mA h g⁻¹ at 20 mA g⁻¹ and displays excellent cycling performance, retaining 94.7% of its capacity throughout 300 cycles at 200 mA g⁻¹.

Structure design

The K layered oxides prepared by solid-state methods typically exhibit a flake-like morphology, which usually face some shortcomings including stress concentration, limited contact area, and slow kinetics^[121]. Designing cathodes with a distinctive morphology and nano-structure is advantageous in reducing the diffusion barrier of K^+ , enhancing the electrode/electrolyte contact area, and mitigating volume variation, leading to improved overall performance^[122,123].

A layered $K_{0.7}Fe_{0.5}Mn_{0.5}O_2$ nanowire structure was designed via the electrospinning method and sintering^[124]. Benefiting from the special interconnected nanowire, it contributes a fast electron/ K^+ transport channel and a large contact area between electrode and electrolyte, promoting a good rate performance [Figure 10A]. Apart from nanowire structures, some other morphologies such as microspheres^[44,125,126], nanosheets^[127,128] and microcubes^[129] also exhibit a similar effect. The hierarchical structure provides a reliable pathway for K^+ ion and electron transportation, as well as buffering the mechanical strain resulting from K^+ ion extraction and insertion. $K_{0.65}Fe_{0.5}Mn_{0.5}O_2$ microspheres were designed through the solvent-thermal method^[45]. The

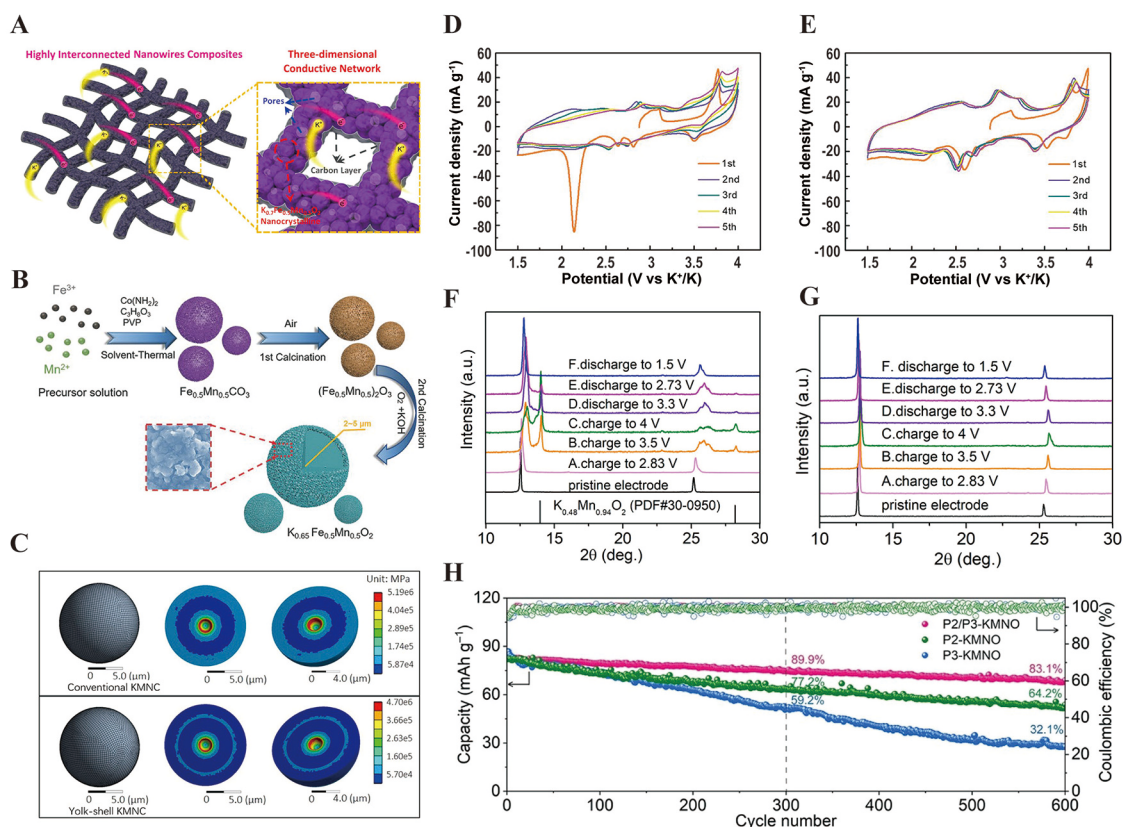


Figure 10. (A) Schematic illustrations of the interconnected $\text{K}_{0.7}\text{Fe}_{0.5}\text{Mn}_{0.5}\text{O}_2$ nanowires^[124]. Reprinted with permission from Ref.^[124]. Copyright 2016 American Chemical Society^[124]. (B) Schematic illustration for the synthesis of uniform P2-type $\text{K}_{0.65}\text{Fe}_{0.5}\text{Mn}_{0.5}\text{O}_2$ microspheres with hierarchical structure^[45]. Reprinted with permission from Ref.^[45]. Copyright 2018 Wiley-VCH^[45]. (C) The finite element model for strain variation during volume expansion^[130]. Reprinted with permission from Ref.^[130]. Copyright 2021 Wiley-VCH^[130]. Cyclic voltammetry of (D) S-KMO electrode and (E) AlF_3 @S-KMO electrode^[132]. (D and E) Figures Reprinted with permission from Ref.^[132]. Copyright 2019 Wiley-VCH^[132]. Ex situ XRD patterns of (F) H- $\text{K}_{0.7}\text{MnO}_2$ and (G) H- $\text{K}_{0.7}\text{Mn}_{0.7}\text{Mg}_{0.3}\text{O}_2$ ^[133]. (F and G) Figures reprinted with permission from Ref.^[133]. Copyright 2020 Elsevier^[133]. (H) Long-term cycling stability under 1 C of three compounds^[134]. Reprinted with permission from Ref.^[134]. Copyright 2024 Wiley-VCH^[134].

compact and uniform hierarchical microspheres effectively sustain the stress resulting from volume changes during K^+ extraction and insertion, and hasten the diffusion kinetics of K^+ by shortening the diffusion distances [Figure 10B]. The cathode delivers an initial specific capacity of about 151 mA h g^{-1} at an average potential of 2.5 V (vs. K/K^+), within the range of 1.5 and 4.2 V at 20 mA g^{-1} . Similarly, compared with irregular $\text{K}_{0.5}\text{Mn}_{0.8}\text{Co}_{0.1}\text{Ni}_{0.1}\text{O}_2$, the $\text{K}_{0.5}\text{Mn}_{0.8}\text{Co}_{0.1}\text{Ni}_{0.1}\text{O}_2$ microcuboid exhibits higher surface area with mesopores, which facilitates ion diffusion^[129]. Micropores usually show high surface area but may hinder K^+ ion diffusion due to size constraints. Macropores enable rapid ion transport but sacrifice capacity owing to the reduced active sites. Mesoporous materials are often seen as the optimal solution for balancing capacity, rate and stability. The Yolk-Shell $\text{K}_{0.5}\text{Mn}_{0.85}\text{Ni}_{0.1}\text{Co}_{0.05}\text{O}_2$ was synthesized by co-precipitation method with a high specific capacity and excellent cycling performance, which displays the initial capacity of 106 mA h g^{-1} at 20 mA g^{-1} corresponding 0.43 K^+ insertion in per formula unit and 80.5% capacity retention after 400 cycles at 200 mA g^{-1} ^[130]. The strain simulation shows that the yolk-shell structure experiences a lower internal strain throughout the sphere with volume changes benefiting excellent battery performance [Figure 10C].

It is well known that polycrystalline cathode materials are susceptible to cracking due to the uneven distribution of stress on primary particles. Furthermore, the restricted exposure of certain crystal planes hinders the diffusion kinetics in polycrystalline cathodes, resulting in inferior rate performance. Conversely, single-crystal materials benefit from their inherent structural integrity, effectively mitigating structural cracking, while also promoting ion diffusion kinetics through the controlled growth of specific crystal planes. Lv *et al.* employed the synergistic effect of Fe and Cu elements to synthesize a single-crystal $\text{K}_{0.35}\text{Mn}_{0.8}\text{Fe}_{0.1}\text{Cu}_{0.1}\text{O}_2$ (KMCFO) cathode, which exhibits a high cycling stability and an outstanding rate performance^[131]. The SEM images confirmed the highly ordered single-crystal structure, which grows along (001) crystal plane. Further, a single-phase reaction was observed in KCFMO during de/potassiation without a P3-O3 phase transition, illustrating excellent stability.

Combining morphology design and surface coating can prevent side reactions at the interface and enhance structural stability during the charging/discharging process. The strong cationic peak at 2.14 V of $\text{K}_{1.39}\text{Mn}_3\text{O}_6$ (S-KMO) during the first cycle was not subsequently observed, which relates to the irreversible structural transition induced by K^+ ion insertion^[132]. Conversely, the CV curve of AlF_3 -coated $\text{K}_{1.39}\text{Mn}_3\text{O}_6$ microsphere (AlF_3 @S-KMO) shows better overlap than S-KMO and more oxidation-reduction peaks than bulk $\text{K}_{1.39}\text{Mn}_3\text{O}_6$, suggesting a higher specific capacity for AlF_3 @S-KMO [Figure 10D and E]. The AlF_3 -coated $\text{K}_{1.39}\text{Mn}_3\text{O}_6$ microsphere (AlF_3 @S-KMO) cathode delivers a first discharge capacity of 112 mA h g^{-1} at 1.5–4 V at 10 mA g^{-1} and better cycling stability. The variation of lattice spacing proved that the coating layer effectively prevents significant structural change during the K^+ extraction and insertion process, thereby enhancing the structural stability of layered oxides. Designing hierarchical structures typically accelerates ion diffusion rates, improving kinetic performance, but thermodynamic phase transitions may not necessarily be resolved. Thus, overall performance may be improved by simultaneously employing element doping and morphology optimization. Weng *et al.* prepared hierarchical $\text{K}_{0.7}\text{Mn}_{0.7}\text{Mg}_{0.3}\text{O}_2$ microparticles (H-KMMO) and hierarchical $\text{K}_{0.7}\text{MnO}_2$ (H-KMO)^[133]. It was found that a phase transition occurs in the XRD pattern of H-KMO when charged to high voltage; in contrast, H-KMMO maintains its original structure throughout the entire charge-discharge process, indicating the Mg substitution successfully suppressed phase transition and enhanced structural stability [Figure 10F and G]. Additionally, a higher K^+ ion diffusion coefficient is exhibited in the Mg-doped cathode, which can be attributed to the suppression of phase transition reducing the ion diffusion barrier.

Within potassium-layered oxides, P2-type materials generally demonstrate better structural stability because of their mirror-symmetric structure, while P3-type materials commonly exhibit high specific capacity. Consequently, multiphase composite structures have been designed to harness the synergistic benefits of each phase, achieving superior electrochemical performance^[134]. Liu *et al.* have achieved a series of $\text{K}_{0.67-x}\text{Na}_x\text{Ni}_{0.17}\text{Co}_{0.17}\text{Mn}_{0.66}\text{O}_2$ ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$) by a co-precipitation followed by solid-state reaction^[135]. XRD analysis reveals the formation of a P3-K/P2-Na composite when $x > 0.1$. Notably, at a sodium substitution level of 0.3, the composite demonstrates improved cycling performance (capacity retention of 93% after 100 cycles at 20 mA g^{-1}). Recently, a P2/P3 composite $\text{K}_{0.7}\text{Mn}_{0.67}\text{Ni}_{0.33}\text{O}_2$ (KNMO) was achieved through electrochemical ion exchange with sodium layered oxide. The cathode achieves a notable capacity of 116.3 mA h g^{-1} at 10 mA g^{-1} and sustains 83.1% capacity retention throughout 600 cycles at 100 mA g^{-1} , attributable to the synergistic interplay between the two phases [Figure 10H]. *In-situ* XRD analysis indicates that P3-KMNO undergoes a P3-O3 phase transition when charging to 4 V. Conversely, the phase transition is effectively restrained in the composite, illustrating that the composite cathode is more suitable for cycling^[134].

Electrolyte optimization

The electrolyte in PIBs plays a pivotal role in dictating the electrochemical performance of layered oxide cathodes. It governs K^+ ion transport kinetics, interfacial stability, and the formation of a stable CEI, which directly impacts capacity retention, rate capability, and cycle life^[136,137]. Currently, carbonate-based electrolyte such as 0.8 M KPF₆ in EC:DEC (1:1) is the most popular electrolyte for PIBs. It is noted that, however, He *et al.* reported that the highly reactive K metal may react with conventional carbonate solvent resulting in a low CE^[138]. Besides, high-voltage electrolytes for layered oxides are still lacking, constraining the performance of electrodes. Therefore, electrolyte optimization, including high-concentration electrolyte (HCEs), locally HCEs, and electrolyte additives, has been widely studied, which are mainly focused on forming a robust CEI.

An inorganic-rich CEI is usually regarded as more stable than an organic CEI because of its high mechanical strength and poor solubility in organic electrolytes. Recently, Zhao *et al.* reported a high-concentration electrolyte [3 M KFSI in trimethyl phosphate (TMP)]^[139]. The Raman spectra results identified that there are more contact ion pairs (CIP) and aggregate clusters (AGG) in the TMP-based electrolyte, reducing free solvent molecules and promoting robust inorganic-rich CEI [Figure 11A]. The thin and uniform CEI maintained the long cycling stability for the cathode (85.1% capacity retention at 10 mA g⁻¹ after 100 cycles). Similarly, a triethyl phosphate (TEP)-based electrolyte (2 M KFSI in TEP) formed a robust KFSI salt-derived SEI film with a uniform thickness, which efficiently suppresses the decomposition of the solvent and passivates the anode with a high CE of 99.6%^[140]. Building on the success of HCEs, localized HCEs (LHCEs) that combine a moderate salt concentration with a diluent to create a “localized” high-ion density environment have emerged as a refined strategy to balance ionic conductivity, cost, and CEI stability. Using (1,1,2,2,5,5,6,6-octafluoro-3-oxahexane) OHE as a diluent, the 0.6 M KFSI in tris(1-propyl) phosphate (TPP):tris(2,2,2-trifluoroethyl) phosphate (TFP):OHE (4:1:5) electrolyte retains an average CE of 99.45% and achieves a capacity retention of 80% after 2,000 cycles in K||FeHCF cell^[141]. However, diluents are generally costly and environmentally unfriendly, which hamper its scalability.

The weakly coordinated solvent, which facilitates the occupation of anions within the primary solvation structure, enhances the inorganic composition of the CEI. Gu *et al.*, employing a long chain linear ether [dipropylene glycol dimethyl ether (DPGDME)] along with a weakly coordinated solvent [ethylene glycol dibutyl ether (DBE)], prepared 1.5 M KFSI-DPGDME/DBE (designed as MB)^[142]. Owing to the special solvation structure, the oxidation potential is promoted to 4.94 V higher than that of a common electrolyte. The results of in-depth XPS further confirm that there are more decompositions of FSI⁻ anions, which possessed high electron conductivity and mechanical strength [Figure 11B]. The transmission electron microscopy (TEM) images illustrate that the MB electrolyte facilitates the formation of a thin and homogeneous CEI, promoting rapid interfacial kinetics. Due to the strong electronegativity of fluorine atoms, fluorine-containing solvents generally have weaker coordination with K^+ ions, thus encouraging the participation of more anions in interphase formation^[143,144]. The linear sweep voltammetry (LSV) test results for 0.8 M KFSI in TFP reveal a cutoff voltage of up to 4.95 V, significantly higher than that of conventional electrolytes. Moreover, compared to 0.8 M KPF₆ in EC:DEC (1:1), the interphase formed on the electrode surface by 0.8 M KFSI in TFP shows a stable morphology after cycling, which ensures the cathode stability over long cycles [Figure 11C and D]^[143].

Certain beneficial electrolyte additives such as lithium difluoro(oxalate) borate (LiDFOB), KNO₃ and AlCl₃, also have a positive effect in enhancing the interphase stability, thereby contributing to improved performance^[145-148]. The K_{0.49}MnO₂ cathode employing 0.8 M KPF₆ in EC:DEC (1:1) with 0.7 wt% LiDFOB (BE-LiDFOB) as electrolyte exhibits a superior capacity (more than 120 mA h g⁻¹ at 20 mA g⁻¹ between 1.5-4 V) and an excellent cycling performance (78.6% capacity retention over 300 cycles relative to the

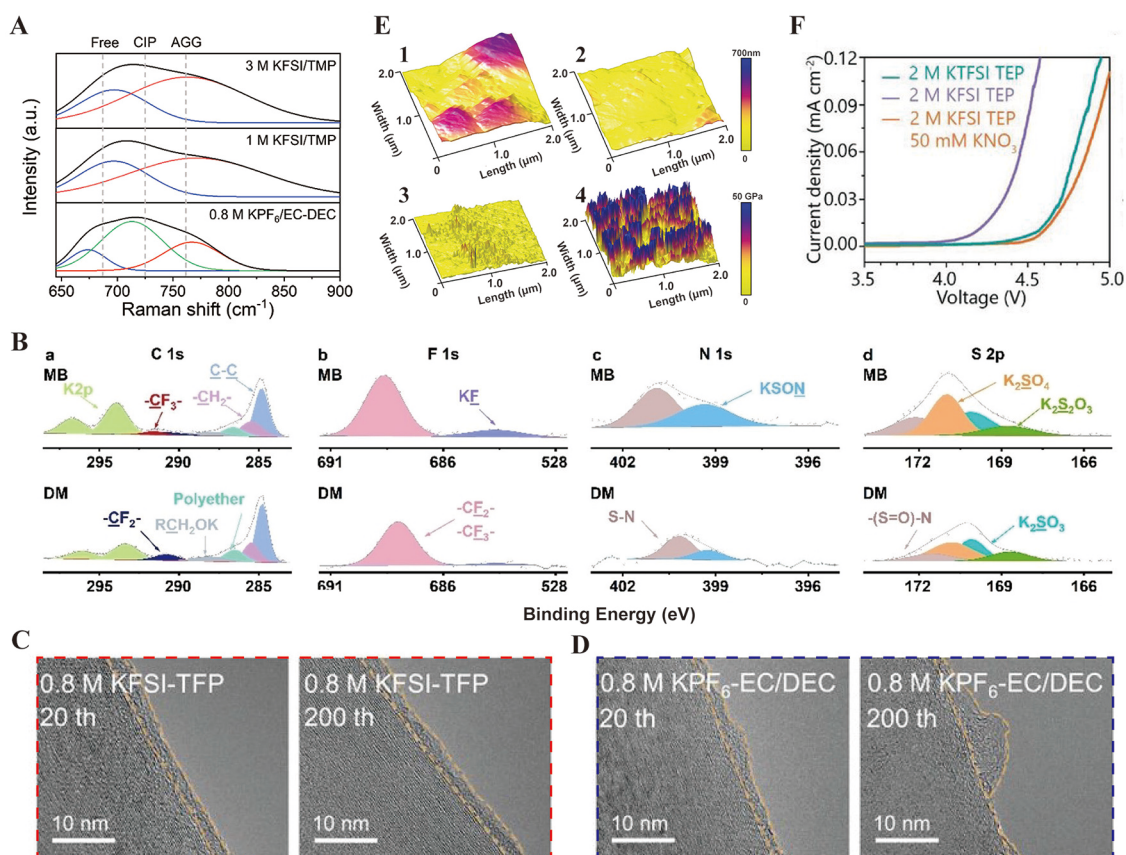


Figure 11. (A) Raman spectra of three electrolytes^[139]. Reprinted with permission from Ref.^[139]. Copyright 2024 Wiley-VCH^[139]. (B) XPS spectra of C 1s, F 1s, N 1s, and S 2p on $K_{0.67}MnO_2$ surface^[142]. Reprinted with permission from Ref.^[142]. Copyright 2024 Wiley-VCH^[142]. (C and D) TEM images of SEI on the graphite cycled in 0.8 M KFSI-TFP (C) and 0.8 M KPF_6 -EC/DEC (D) for 20 and 200 cycles^[143]. (C and D) Figures reprinted with permission from Ref.^[143]. Copyright 2023 Wiley-VCH^[143]. (E) AFM images and surface modulus distribution of $K_{0.5}MnO_2$ surface cycled in (E1, E3) BE and (E2, E4) BE-LiDFOB electrolytes^[145]. Reprinted with permission from Ref.^[145]. Copyright 2024 Wiley-VCH^[145]. (F) LSV curves of electrolytes of nitrate-free electrolyte, nitrate-containing electrolyte and KTFSI electrolyte in K||Al cells^[146]. Reprinted with permission from Ref.^[146]. Copyright 2024 Wiley-VCH^[146].

second cycle)^[145]. The Atomic Force Microscopy (AFM) images of the cathode surface cycled in BE and BE-LiDFOB show that a thin and homogeneous CEI layer was formed in the modified electrolyte, which enhances charge transfer. What is more, the CEI with a BE-LiDFOB electrolyte exhibits better mechanical strength than BE, demonstrating it can effectively suppress volume expansion and Mn dissolution [Figure 11E]. Besides enhancing the properties of the interphase, additives can also improve the stability during high-voltage operation. The oxidation voltage of 2 M KFSI-TEP electrolyte modified with KNO_3 can reach 4.4 V [Figure 11F], enabling the K||PBAs cell to stably operate in the voltage range of 2-4.3 V for eight months^[146].

SUMMARY AND PERSPECTIVES

PIBs are emerging as promising substitutes for LIBs due to the abundant potassium resources available. However, the K layered oxide cathodes have shown unsatisfactory electrochemical performance [Table 1]. The ideal layered oxide cathode for PIBs should meet the following characteristics: (1) high structural reversibility to minimize phase transition and lattice strain during K^+ ions (de)intercalation; (2) High voltage operation through transition metal coordination optimization to achieve high energy density; (3) Air stability to prevent moisture-induced K^+/H^+ exchange and structural degradation during ambient

Table 1. A summary of the electrochemical performance of K layered oxide cathodes

Strategy	Cathode	Voltage window	Specific capacity/ mA h g^{-1} (current density/ mA g^{-1})	Capacity retention/ (cycles, current density/ mA g^{-1})
Surface modification	$\text{K}_{0.5}\text{MnO}_2 @ \text{Al}_2\text{O}_3$ [73]	1.5–4 V	127.6 (20)	53% (300, 50)
	$\text{K}_{0.5}\text{Ni}_{0.1}\text{Mn}_{0.9}\text{O}_2 @ \text{FePO}_4$ [74]	1.5–3.9 V	134.7 (20)	85% (500, 500)
	$\text{K}_{0.5}\text{Mn}_{0.8}\text{Co}_{0.2}\text{O}_2 @ \text{K}_3\text{PO}_4 / \text{MnPO}_4$ [114]	1.5–3.9 V	101.3 (100)	80% (500, 1,000)
	$\text{K}_{0.5}\text{Mn}_{0.9}\text{Ti}_{0.1}\text{O}_2 @ \text{CaTiO}_3$ [115]	1.5–3.9 V	119.3 (20)	94.7% (300, 200)
	$\text{K}_{0.5}\text{Mn}_{0.85}\text{Co}_{0.1}\text{Fe}_{0.05}\text{O}_2 @ \text{KMn}_4(\text{PO}_4)_3$ [118]	1.5–4 V	100.5 (20)	72.97% (500, 200)
	$\text{K}_{1.39}\text{Mn}_3\text{O}_6 @ \text{AlF}_3$ [132]	1.5–4 V	110 (10)	94.9% (100, 50)
	$\text{K}_{0.5}\text{MnO}_2 @ \text{KTaO}_3$ [119]	1.5–3.9 V	82.07 (400)	98.1% (100, 100)
Structure design	P3- $\text{K}_{0.5}\text{MnO}_2$ microsphere [44]	1.5–3.9 V	104 (10)	89.1% (400, 200)
	P3/P2- $\text{K}_{0.37}\text{Na}_{0.3}\text{Ni}_{0.17}\text{Co}_{0.17}\text{Mn}_{0.66}\text{O}_2$ [135]	2–4.2 V	86.12 (20)	91.5% (100, 20)
	P2- $\text{K}_{0.65}\text{Fe}_{0.5}\text{Mn}_{0.5}\text{O}_2$ microsphere [45]	1.5–4.2 V	151 (20)	78% (350, 100)
	P2- $\text{K}_{0.6}\text{CoO}_2$ microsphere [121]	1.7–4 V	82 (10)	87% (300, 40)
	Hierarchical $\text{K}_{0.7}\text{Mn}_{0.7}\text{Mg}_{0.3}\text{O}_2$ [133]	1.5–4 V	144.5 (20)	82.5% (400, 100)
	P3- $\text{K}_{0.5}\text{Mn}_{0.8}\text{Ni}_{0.1}\text{Co}_{0.1}\text{O}_2$ microcuboid [129]	1.5–4 V	94.5 (20)	61% (300, 100)
	P3- $\text{K}_{0.45}\text{Mn}_{0.5}\text{Co}_{0.5}\text{O}_2$ peanut [127]	1.2–3.9 V	123.2 (20)	73.8% (300, 300)
	P2- $\text{K}_{0.6}\text{CoO}_2$ microcube [122]	1.7–4 V	87.2 (20)	86.9% (1,000, 40)
	P'3- $\text{K}_{0.35}\text{Mn}_{0.8}\text{Fe}_{0.1}\text{Cu}_{0.1}\text{O}_2$ (single crystalline) [131]	1.5–3.9 V	96.8 (50)	91.1% (500, 500)
	P2/P3- $\text{K}_{0.7}\text{Mn}_{0.67}\text{Ni}_{0.33}\text{O}_2$ [134]	1.5–4 V	116.3 (10)	83.1% (600, 100)
Element doping	O3/P2/P3- $\text{Na}_{0.9}\text{Ni}_{0.3}\text{Mn}_{0.55}\text{Cu}_{0.1}\text{Ti}_{0.05}\text{O}_2$ [161]	1.5–4 V	108 (15)	83% (600, 300)
	P3- $\text{K}_{0.5}\text{Mn}_{0.8}\text{Fe}_{0.1}\text{Ni}_{0.1}\text{O}_2$ [79]	1.5–3.9 V	120 (50)	74% (300, 50)
	P3- $\text{K}_{0.5}\text{Ni}_{0.1}\text{Mn}_{0.9}\text{O}_2$ [24]	1.5–3.9 V	121 (10)	82% (100, 100)
	P3- $\text{K}_{0.54}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ [82]	1.5–3.9 V	120.4 (20)	62% (500, 20)
	$\text{K}_{0.28}\text{MnO}_2 \cdot 0.15\text{H}_2\text{O}$ [100]	1.4–3.6 V	152 (15)	81% (100, 15)
	P2- $\text{K}_{0.44}\text{Ni}_{0.22}\text{Mn}_{0.78}\text{O}_2$ [41]	1.5–4 V	125.5 (10)	67% (500, 200)
	P3- $\text{K}_{0.45}\text{Ni}_{0.1}\text{Co}_{0.1}\text{Al}_{0.05}\text{Mn}_{0.75}\text{O}_2$ [166]	1.5–4 V	84.5 (20)	77.4% (100, 20)
	P3- $\text{K}_{0.67}\text{Mn}_{0.83}\text{Ni}_{0.17}\text{O}_2$ [42]	1.5–3.8 V	122 (20)	75% (200, 500)
	$\text{K}_{5/9}\text{Mn}_{7/9}\text{Ti}_{2/9}\text{O}_2$ [91]	1.5–4.2 V	135 (20)	70% (100, 100)
	P'3- $\text{K}_{0.3}\text{Mn}_{0.9}\text{Cu}_{0.1}\text{O}_2$ [111]	1.5–3.9 V	124 (10)	82% (50, 100)
	P3- $\text{K}_{0.5}\text{Mn}_{0.6}\text{Co}_{0.2}\text{Fe}_{0.1}\text{Mg}_{0.1}\text{O}_2$ [92]	1.5–3.9 V	104.6 (50)	91% (150, 100)
	P3- $\text{K}_{0.4}\text{Mn}_{0.8}\text{Fe}_{0.1}\text{Ti}_{0.1}\text{O}_2$ [86]	1.8–4 V	117 (20)	74% (300, 200)
	P3- $\text{K}_{0.45}\text{Co}_{1/12}\text{Mg}_{1/12}\text{Mn}_{5/6}\text{O}_2$ [157]	1.5–3.9 V	98 (120)	54.8% (500, 1,000)
	P3- $\text{K}_{0.54}\text{Mn}_{0.78}\text{Mg}_{0.22}\text{O}_2$ [90]	1.5–4 V	132.4 (20)	84% (100, 200)

$P3\text{-K}_{0.45}\text{Rb}_{0.05}\text{Mn}_{0.85}\text{Mg}_{0.15}\text{O}_2$ [104]	1.5-3.9 V	108.0 (20)	98.2% (200, 200)
$\text{K}_{0.4}\text{Fe}_{0.1}\text{Mn}_{0.8}\text{Ti}_{0.1}\text{O}_2 \cdot 0.16\text{H}_2\text{O}$ [61]	1.8-4 V	116 (20)	90% (1,000, 2,000)
$P3\text{-K}_{0.45}\text{Mn}_{0.9}\text{Al}_{0.1}\text{O}_2$ [112]	1.5-3.9 V	152 (20)	67% (1,000, 500)
$P'3\text{-K}_{0.6}\text{MnO}_{1.97}\text{F}_{0.03}$ [96]	1.5-3.9 V	111 (10)	77.3% (100, 100)
$\text{K}_{0.4}\text{Mn}_{0.9}\text{Li}_{0.1}\text{O}_2 \cdot 0.33\text{H}_2\text{O}$ [102]	1.5-4 V	101.87 (20)	84.04% (100, 100)
$P2\text{-K}_{0.02}\text{Na}_{0.55}\text{Mn}_{0.7}\text{Ni}_{0.25}\text{Zn}_{0.05}\text{O}_2$ [167]	1.5-4 V	57 (100)	97% (1,000, 100)
$P3\text{-K}_{0.6}\text{Ni}_{0.05}\text{Fe}_{0.05}\text{Mg}_{0.05}\text{Ti}_{0.05}\text{Mn}_{0.0725}\text{O}_2$ [108]	1.5-3.9 V	39.3 (2,000)	87.5% (600, 1,000)
$P3\text{-K}_{0.7}\text{Fe}_{0.05}\text{Co}_{0.1}\text{Mn}_{0.75}\text{Ni}_{0.05}\text{V}_{0.05}\text{O}_2$ [106]	1.5-3.9 V	77.39 (1,000)	70.3% (500, 1,000)
$P3\text{-K}_{0.45}\text{Mn}_{0.6}\text{Ni}_{0.075}\text{Fe}_{0.075}\text{Co}_{0.075}\text{Ti}_{0.1}\text{Cu}_{0.05}\text{Mg}_{0.025}\text{O}_2$ [107]	1.5-4.2 V	106.8 (10)	60.4% (200, 100)
$P3\text{-K}_{0.5}\text{Mn}_{0.8}\text{Co}_{0.2}\text{B}_{0.1}\text{O}_2$ [98]	1.4-4 V	121.4 (10)	87.1% (100, 200)
$P'3\text{-K}_{0.5}\text{Mn}_{0.8}\text{Cu}_{0.1}\text{Mg}_{0.1}\text{O}_2$ [89]	1.5-4 V	100.1 (10)	75.41% (100, 50)
$P3\text{-K}_{0.39}\text{Mn}_{0.77}\text{Ni}_{0.23}\text{O}_{1.9}\text{F}_{0.1}$ [95]	1.5-4 V	93.5 (20)	77% (350, 100)
$P3\text{-K}_{0.5}\text{Mn}_{0.8}\text{Co}_{0.1}\text{Zn}_{0.1}\text{O}_2$ [168]	1.5-3.9 V	105 (100)	89.8% (100, 100)
$P3\text{-K}_{0.57}\text{Cu}_{0.1}\text{Fe}_{0.1}\text{Mn}_{0.8}\text{O}_2$ [169]	1.5-4.2 V	135 (20)	68% (500, 200)
$P3\text{-K}_{0.5}\text{Mn}_{0.87}\text{Co}_{0.05}\text{Fe}_{0.05}\text{Li}_{0.03}\text{O}_2$ [94]	1.5-4 V	107.1 (20)	88.5% (300, 200)
$P3\text{-K}_{0.67}\text{Li}_{0.07}\text{Mn}_{0.93}\text{O}_2$ [93]	1.5-4 V	84.3 (10)	81.3% (100, 50)
$P2\text{-K}_{0.6}\text{Mn}_{0.8}\text{Ni}_{0.1}\text{Ti}_{0.1}\text{O}_2$ [170]	1.5-4.2 V	118 (10)	88% (100, 200)
$P3\text{-K}_{0.5}\text{Mg}_{0.15}\text{Mn}_{0.8}\text{Mg}_{0.05}\text{O}_2$ [103]	1.4-4 V	102.0 (10)	48.2% (400, 100)
$P2\text{-K}_{0.56}\text{Na}_{0.11}\text{Li}_{0.12}\text{Ni}_{0.22}\text{Mn}_{0.66}\text{O}_2$ [46]	1.5-4.6 V	90.2 (20)	89.6% (150, 20)

storage; (4) Excellent electronic/ionic conductivity to enable fast K^+ diffusion kinetics; and (5) Robust surface to block electrolyte corrosion and mitigate interfacial side reactions. In this review, the critical issues for K layered oxide cathodes are systematically discussed, including irreversible phase transition, air instability and interfacial instability. Additionally, the corresponding strategies encompassing element doping, surface modification, structural design, and electrolyte optimization have also been provided. More specifically, element doping primarily aims to inhibit phase transitions and the Jahn-Teller effect of Mn^{3+} , although some literature also reports that doped elements can be involved in forming interfacial films to enhance interface characteristics. Surface modification is focused on suppressing side reactions at the interface and the dissolution of transition metals to improve interfacial properties. Structural design emphasizes reducing the structural stress generated by volume expansion and improving ion transport kinetics. Electrolyte optimization seeks to improve the properties of the CEI, reducing the dissolution of transition metals for enhanced structural stability.

While significant progress has been made in K layered oxide research, the field is still in its early stages, with incomplete understanding of the underlying mechanisms. The kinetics evolution at the interface and the relationship between material structure and performance still require further investigation. To address this, advanced *in-situ/ex-situ* characterization techniques and machine learning-guided simulations should be prioritized to map the kinetics evolution

at interfaces and establish structure-property correlations^[149,150]. Besides, despite K metal sharing a comparable standard hydrogen electrode potential with Li metal, its high atomic weight results in a lower specific capacity. Importantly, many K layered oxides exhibit potassium deficiency, further compromising their electrochemical performance. Emerging strategies such as pre-potassiation or using potassium-rich self-sacrificial additives (e.g., $\text{K}_2\text{C}_4\text{O}_4$) could mitigate the inherent potassium deficiency in layered oxides^[14,151]. The coin cell tests for PIBs are typically conducted over a wide voltage range (1.5–4 V) to maximize capacity. However, the lower discharge voltage necessitates the occurrence of $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox, potentially weakening structural stability due to the Jahn-Teller effect of high-spin Mn^{3+} . Elemental doping (e.g., Mg^{2+} , Ti^{4+}) and the adoption of elements with high redox voltage (eg. Ni^{2+} , Fe^{3+}) can effectively improve material stability and operating voltage. Moreover, while K layered oxides are predominantly synthesized via a solid-state method, alternative routes such as co-precipitation^[37,129,152,153], sol-gel^[154–157], and ion exchange^[134,158–161] could provide novel insights and drive the progress of K layered oxides. Another critical aspect is the electrolyte. Cells assembling K//K layered oxides with carbonate-based electrolytes often exhibit low CE and struggle to cycle reliably above 4 V limiting their performance. Oxygen redox chemistry, extensively studied in LIBs and SIBs, remains underexplored in PIBs due to its activation at higher voltage^[162,163]. Fluorinated electrolytes or (localized) HCEs could enhance oxidation stability and CE, enabling better performance. Notably, the role of polymeric binders in stabilizing the electrochemical performance of layered oxides is often overlooked. The electrochemical stability of binders at high voltage and adhesion during prolonged K^+ insertion/extraction have a significant impact on the performance of the electrodes. It is worth investing efforts to study the relationship between cathode performance and binder and to develop better binders. Furthermore, in terms of commercialization, potassium-layered oxides still have a long journey ahead. It is necessary to recognize that there are substantial performance differences between full and half cells. Metal potassium is typically avoided as the counter electrode in full cells, as the uneven deposition of potassium can lead to dendrite growth, posing a safety hazard to the battery^[164,165]. Transitioning from K-metal to pre-potassiated hard carbon anodes in full cells can circumvent dendrite risks. Moreover, the relatively low specific capacity of potassium also, to some extent, hampers its development. Layered oxides are promising for mid-term applications (e.g., grid storage) if electrolyte compatibility and structural degradation hurdles are addressed. Their commercialization hinges on breakthroughs in air-stable synthesis, low-cost electrolytes, and industry adoption of PIBs as a complement - not replacement - for LIBs. In the future, it is worth investing more effort into exploring the mechanisms of bulk-phase structural evolution, interfacial reaction mechanisms, and innovative synthesis methods, coupled with advanced characterization techniques, to enable rational design of higher-performance layered cathode materials.

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Availability of data and materials

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Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

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