Nano Polymorphism-Enabled Redox Electrodes for Rechargeable Batteries

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Nano polymorphism (NPM), as an emerging research area in the field of energy storage, and rechargeable batteries, have attracted much attention recently. In this review, the recent progress on the composition and formation of polymorphs, and the evolution processes of different redox electrodes in rechargeable metal-ion, metal–air, and metal–sulfur batteries are highlighted. First, NPM and its significance for rechargeable batteries are discussed. Subsequently, the current NPM modulation strategies of different types of representative electrodes for their corresponding rechargeable battery applications are summarized. The goal is to demonstrate how NPM could tune the intrinsic material properties, and hence, improve their electrochemical activities for each battery type. It is expected that the analysis of polymorphism and electrochemical properties of materials could help identify some “processing–structure–properties” relationships for material design and performance enhancement. Lastly, the current research challenges and potential research directions are discussed to offer guidance and perspectives for future research on NPM engineering.

1. Introduction

Polymorphism, the ability of solid materials to form more than one crystal phase, is a characteristic of a wide range of materials, such as polymers, minerals, and metals, that enriches their functionalities for numerous applications. When the structural dimensions of materials are decreased to the nanoscale, the high surface aspect ratio generates additional engineerable space, which enables the polymorphism of nanomaterials. Recently, nano polymorphism (NPM) has been emerging as a topic of interest in the energy storage field, and research is expected to identify and rationally exploit the “processing–structure–properties” relationships of functional materials of interest in the context of the emerging rechargeable battery applications, particularly for cathode and anode materials.

To date, the research on the NPM of rechargeable battery electrodes has achieved significant progress.[1–3] Many electrode materials with various polymorphs, such as traditional layered metal oxides and some emerging types of graphene-like nanosized materials, have been intensively investigated for improving the electrochemical performance of batteries. Moreover, the in-depth underlying storage mechanisms of different polymorphs have been fully or partly revealed using advanced in situ characterization techniques. Based on the previously reported theoretical and experimental results, some potential structural
Optimization strategies for desired polymorphs for specific battery and electrolyte systems could be predicted to accommodate the intercalation-deintercalation process during repeated charging-discharging cycling, which will greatly promote the research progress toward practical battery applications.[4] To date, depending on the NPM design, many nanomaterials have been demonstrated to present attractive electrochemical properties for electrodes in different battery systems. However, these materials are still unable to meet the industrial requirements for the rational combination toward the synergistic effect on the capacity, cycle life, rate capability, damage tolerance, poison resistance, corrosion allowance, safety concerns, and mechanical robustness of batteries. Typically, the primary reasons that could lead to the decrease in the rate capacity and cycling stability of batteries can be classified into: i) irreversible structural phase transition of electrode materials, which is typically accompanied by the migration of transition metal ions; ii) irreversible volume change ratio caused by the repeated insertion and deinsertion of metal ions; iii) irreversible loss of active species (e.g., Li⁺, Na⁺, and S) owing to dendrite growth, unexpected dissolution, and potential side reactions; iv) irreversible loss of oxygen species from the lattice of the cathode materials, leading to the formation of oxygen vacancies; and v) irreversible reactions that originate from electrolytes, such as the undesired decomposition of electrolyte molecular, particularly at high working voltages or rates. Most of these concerns involve the polymorphism of the target electrode materials, particularly the intrinsic polymorph transition process in specific cell configurations with given electrolyte systems. It is expected that the in-depth understanding of the NPM of electrode materials should be a crucial prerequisite for elucidating the phase transition process and subsequent phase modulation strategies required to address irreversible phase transition issues. The two common regulation strategies consist of further promoting the reversible phase transition and partly suppressing the irreversible phase transition. From the viewpoint of achieving desired battery performance, boosting the reversibility of the redox polymorphism, such as the typical reversible intercalation, transformation, transition between ion-rich and ion-poor phases, and transition of multiphase process upon charge and discharge, is a crucial aspect (Figure 1a).[5] Hence, because NPM confers an extra rhythm in tuning the functional properties of electrodes from the perspective of their size, shape, and composition, for boosting the electrochemical performance of batteries, the research on NPM for rechargeable batteries is of great significance.

The champion devices for next-generation energy storage technologies remain elusive but promising. As mentioned above, a comprehensive and in-depth understanding of the NPM of electrode materials is essential for effectively overcoming the drawbacks of efficient and reliable battery applications. Therefore, a systematic overview of the cutting-edge research on NPM used for promoting desired redox reactions in rechargeable batteries is critical, as it would establish new perspectives that could promote advanced battery science and technology research. The main goal of this review was to highlight the polymorphs of electrode materials and their electrochemical properties and also to identify some “processing-structure-properties” relationships in rechargeable batteries, particularly metal-ion, metal-air, and metal-sulfur batteries (Figure 1b). Herein, we reveal how NPM could tune the intrinsic properties of materials, and, hence, improve their electrochemical activities. First, we introduce the basic background of NPM and highlight the significance of NPM for rechargeable batteries. Subsequently, we summarize the current modulation strategies of different electrode materials using NPM in their respective rechargeable battery application fields. Lastly, we analyze the research gaps and put forward our perspective on the challenges and future research directions in these fields.

2. NPM of Reduction Electrodes

In this section, we present a detailed summary of the NPM manipulation of several representative reduction cathode materials, including Li, Na, K, Zn, Al, O, and S. Considering the complex conditions of O cathodes in metal–air batteries, the NPM control of the discharge products of different types of metal–O₂ batteries were independently analyzed.

2.1. NPM of Li Cathodes

2.1.1. Lithium Transition-Metal Oxides

Currently, lithium transition-metal oxides (LiMO₂) are widely used for commercial consumer electronics. However, their reversible capacities are still limited to less than 200 mAh g⁻¹. Moreover, the transition between the hexagonal and monoclinic phases, which occurs in the range of 4.1–4.2 V, induces unexpected volume expansion. To obtain high-capacity Li-ion batteries (LIBs) and suppress the phase transition process, increasing the Li contents to obtain Li-rich Li₁ₓM₀.₉ₓO₂ and introducing heteroatoms to form multicomponent LiₓMₓM′₁−ₓO₂ species are considered effective solutions. In 2001, when Al was introduced in LiCoO₂ cathodes to form LiCo₁₋ₓAlₓO₂ solid solutions, no transition from the hexagonal to the monoclinic phase was observed,[6] and this greatly increased the voltage and capacity retention. The capacity loss of the modified cathode at 0.5 C after 70 cycles ranged between 4–15%, whereas only 60% of the initial capacity of the LiCoO₂ cathode was retained after 30 cycles. However, typically, this chemical substitution strategy cannot significantly improve the specific capacity (~172–174 mAh g⁻¹ for the LiCo₁₋ₓAlₓO₂ cathode), and can sometimes even induce a capacity loss. Conversely, cathodes with three or more transition metal elements increase the complexity of the phase transition process and their sensitivity to electrolyte systems. For example, LiNi₀.₅Mn₀.₅O₂ and LiNi₀.₅Mn₀.₅Co₀.₅O₂ underwent a progressive surface reconstruction from an R₃m-layered phase to an Fm̅3m rocksalt phase during cycling and/or exposure to electrolytes.[7] Moreover, the Li₀.₁Ni₀.₄Mn₀.₆Co₀.₃O₂ cathode prepared via the chemical delithiation of LiNi₀.₅Mn₀.₅Co₀.₅O₂ underwent a phase transformation from a R₃m-layered phase structure to a reduced mixed spinel/rocksalt structure upon heating.[8] The studies on surface reconstruction and phase evolution offer some clues for the origins of the capacity fading and increase in impedance of layered cathode materials under high voltage or thermal abuse conditions.
2.1.2. Li-Rich Layered Oxides

Li-rich layered oxides, such as Li[Li\(_{1/2-2x/3}\)Ni\(_x\)Mn\(_{2/3-x/3}\)]O\(_2\) (0 < x < 1/3), are high-performance cathode materials with excellent specific capacity of over 250 mAh g\(^{-1}\). Many pioneering research efforts on the original crystal structures of the Li-and-Mn-rich Li\(_{1+x}\)M\(_{1-x}\)O\(_2\) cathode, which were based on experimental neutron and X-ray diffraction (XRD) patterns, concluded that three possible models, namely, the intermixed nanodomains of Li-rich monoclinic Li\(_2\)MnO\(_3\) and Li-depleted trigonal LiMM'\(_x\)O\(_2\) phases and an individual monoclinic or trigonal phase, may exist.\(^9\),\(^10\) Shukla et al. systematically examined the well-formed Li\(_{1.2}\)[Ni\(_{0.13}\)Mn\(_{0.54}\)Co\(_{0.13}\)]O\(_2\) and two commercial materials (TODA HE5050 and HCMR XLE2). They used aberration-corrected scanning transmission electron microscopy (STEM) coupled with advanced electron energy loss spectroscopy, and X-ray energy-dispersive spectroscopy techniques to confirm that the Li-and-Mn-rich bulk was an aperiodic crystal comprising three monoclinic structure variants with a surface layer consisting of a Co- and/or Ni-enriched spinel.\(^11\) Li-rich layered metal oxides with excess Li occupancy can be used to achieve high capacities. However, transition metals migrated toward the neighboring Li slabs during the extraction of Li\(^+\), and thus, caused phase transition into spinel and/or rocksalt structures during cycling. This led to the gradual decrease in both operation voltage and specific capacity during cycling. To stabilize the surface structure of Li-rich oxides and suppress the unexpected phase transition to promote rate capability and cycling stability, surface...
addition to layered oxide structures, olivine lithium iron phosphate (LiFePO4) is another widely studied cathode material for Li storage systems, owing to its low cost and attractive safety features. Despite the intrinsic insulating nature, low electronic conductivity, and poor ionic transport properties of LiFePO4, high operation rates can be easily achieved via particle size reduction, cation doping, and/or conductive carbon coating. A well-known two-phase transformation between the Li-poor FePO4 and Li-rich LiFePO4 phases was observed during Li storage at room temperature, and the presence of a temperature-driven solid solution in LiFePO4 (0 < x < 1) was confirmed at elevated temperatures. Moreover, an alternative single-phase transformation path was observed at a very low overpotential, which could bypass the nucleation and growth of a second phase. Furthermore, metastable solid solution phases based on non-equilibrium thermodynamics were detected for LiFePO4 nano-particle electrodes during high-rate cycling. To date, many pioneering studies have been conducted on the phase transition of LiFePO4 cathodes using different advanced experimental techniques (e.g., in situ XRD, in situ neutron diffraction, in situ transition electron microscopy (TEM), scanning transmission X-ray microscopy, operando X-ray microscopy, hard X-ray microscopy, soft X-ray tomography, X-ray absorption near-edge spectroscopy (XANES), and solid-state nuclear magnetic resonance) and theoretical simulation models (e.g., radial, mosaic, shrinking core, domino-cascade, core–shell, single-phase kinetic, and phase transformation wave). However, the specific phase transition process of such cathode materials has not been elucidated yet. An investigation on the structural evolution of multicomponent olivine materials (LiFe5Mn3Co3−x−yPO4, 0 < x, y < 1) upon delithiation concluded that two competing factors, namely the electrostatic interaction among cations and lattice misfit degree, determined the preference for a two- or one-phase reaction in olivine materials. Recently, Liu et al. have demonstrated that a conductive secondary phase (Fe2P phase) formed on LiFePO4 particles during carbon coating and discovered that the presence of this secondary phase presented a positive effect on the electrochemical performance of LiFePO4 materials. The electrode that featured an optimized amount of Fe2P phase could bypass the nucleation and growth of a second phase. Kim et al. developed a robust surface structure for Li-rich layered oxide cathodes, in which Ni atoms are regularly arranged between transition metal layers, to mitigate the mixing of the transition metals, and thus, suppress unwanted phase transitions. As illustrated in Figure 2a, b, after the first charge, the pristine electrode presented rocksalt- and/or spinel-like phases. In contrast, the modified electrode surface maintained the original layered structure under the same conditions and did not undergo phase transition (Figure 2c). This modification resulted in a high reversible capacity of 218.3 mAh g−1 at a current density of 0.25 A g−1 and a high cycling stability of 94.1% after 100 cycles. To further boost the capacity of Li-rich layered oxides to over 300 mAh g−1, oxygen vacancies were introduced at the surface of the Li-rich layered oxides using a gas–solid interface reaction, which did not affect the structural integrity of the electrodes. Theoretical calculations and experimental results suggested that oxygen vacancies played an important role in facilitating the diffusion of Li+ via the activation of the Li species located in the tetrahedral sites and suppression of the gas at the metal oxide surface. Consequently, a high initial discharge capacity of 301 mAh g−1 and corresponding coulombic efficiency as high as 93.2% were achieved for the target material with surface oxygen vacancies \( \text{Li}[\text{Li}_{0.144}\text{Ni}_{0.136}\text{Co}_{0.136}\text{Mn}_{0.544}]\text{O}_2 \). Moreover, no noticeable voltage decay, which was accompanied by a high reversible capacity of 300 mAh g−1, was observed after 100 discharge–charge cycles. In addition to layered oxide structures, olivine lithium iron phosphate (LiFePO4) is another widely studied cathode material for Li storage systems, owing to its low cost and attractive safety features. Despite the intrinsic insulating nature, low electronic conductivity, and poor ionic transport properties of LiFePO4, high operation rates can be easily achieved via particle size reduction, cation doping, and/or conductive carbon coating. A well-known...
Compared to the aforementioned conventional intercalation cathodes with relatively low specific capacities (>140 and ≈170 mAh g⁻¹ for LiCoO₂ and LiFePO₄, respectively), transition metal oxides or fluorides (TMOs or TMFs, respectively) with much higher specific capacities are promising cathode materials for next-generation high-capacity LIBs.³⁴ Vanadium pentoxide (V₂O₅) and iron(III) fluoride (FeF₃) are representative types of TMO and TMF cathode materials, respectively. Based on the V₂O₅ + 3 Li⁺ + 3 e⁻ ⇄ Li₃V₂O₅ intercalation-type reaction, the theoretical capacity of V₂O₅ was as high as 443 mAh g⁻¹. Similar to most reported metal oxide cathodes, crystalline and amorphous V₂O₅ cathodes undergo structural phase transitions during lithiation–delithiation, which could induce mismatched mechanical strain owing to the coexistence of various phases, and thus, cause irreversible structural damage. In operando synchrotron high-energy X-ray diffraction analysis of vanadium oxide-based cathodes confirmed that the presence of conductive graphene could effectively delay the phase transition temperature of vanadium oxide between disordered and crystalline phases.³⁵

Unlike the intercalation-type V₂O₅ cathode material, FeF₃ is a conversion-type cathode material (FeF₃ + 3 Li⁺ + 3 e⁻ ⇄ 3 LiF + Fe) that can achieve a high Li-storage capacity of 712 mAh g⁻¹. To track the phase evolution of FeF₃ during charging, we used operando hard X-ray spectroimaging, and determined that as the voltage increased the metallic Fe phase was first converted into a Fe²⁺-containing intermediate phase, followed by the slow conversion of the intermediate phase to Fe³⁺ under constant-voltage charging.³⁶ Although the reversibility of Fe-containing TMF cathodes is superior to that of other TMF cathodes, such as copper fluoride (CuF₂), their energy efficiency is still poor owing to the large polarization and cycling hysteresis, which greatly limits their commercial applications. A recent study revealed that ternary metal fluorides that contained both Cu and Fe (CuₓFe₁₋ₓF₂) presented an unexpectedly small hysteresis of less than 150 mV with the reversible redox reactions of Cu and Fe species achieved.³⁴ As illustrated in Figure 2d, the conversion reactions involving the reduction of Cu and Fe species in the CuₓFe₁₋ₓF₂ cathode first occurred during the initial discharge stages (Stages I and II), and two-step reconversion reactions occurred during the subsequent stages. The reconversion of Fe species began with the formation of an iron(II) fluoride (FeF₂) intermediate phase which further transformed into rutile-like iron fluoride. The rutile-like Fe-containing fluoride structure promoted the nucleation and growth of Cu-based fluoride species on the iron fluoride surface, and that led to the formation of a Cu–Fe–F-based rutile-like framework, which was similar to the original structure (Stage III). As the potential further increased, a Cu-deficient phase could finally form, largely owing to traces of irreversible Cu species being dissolved in the electrolyte system or segregated into larger and isolated particles (Stage IV).³⁴

2.1.3. Transition Metal Oxides or Fluorides

2.2. NPM of Na Cathodes

In contrast to the cathodes of LIB systems, Na-based layered oxide cathodes present different stacking structures, owing to the preferred prismatic coordination of Na⁺.³⁷ Typically, a layered structure consists of parallel sheets with edge-sharing TMO octahedra (where TM is a transition metal, such as Co, Fe, Mn, Ni, or V). The main families of Na-based layered oxides are the P2-(e.g., Na₀.₅[Ni₉.₇Fe₀.₃]MO₆) and O3-type (e.g., Na₉CoO₂, Na₉MnO₂, and Na₉Ni₉MnO₆), structures, where O and P denote the octahedral and trigonal prismatic phases, respectively, which host Na⁺ ions, and the numbers 2 and 3 represent the minimum number of TM-O sheets in a single cell unit.³⁸,³⁹ Because the ionic radius of Na⁺ (1.02 Å) is larger than that of Li⁺ (0.76 Å), Na⁺ ions often present sluggish transport kinetics. However, the migration of Na⁺ occurs easier in P-type stacking frameworks than in O-type stacking frameworks. This is largely due to the unique open structures present in the P-type stacking frameworks, which can greatly facilitate the diffusion of Na⁺ ions. Specifically, Na⁺ ions can easily migrate along adjacent prismatic sites with low diffusion barriers and swift ionic transport pathways in P-type layered materials. However, during charging and discharging, this type of cathode materials typically undergoes a phase transition between O- and P-type stacks (O3 ≔ P3 or P2 ≔ O2), which originates from the variable concentration of ions. During the phase transition process, the induced volume change greatly decreases the discharge capacity and restricts the available reversible capacity.

2.2.1. Chemical Substitution

Doping electrochemically inactive elements into P2- and O3-type stacks is an effective strategy that can be used to address the aforementioned concerns and improve the electrochemical performance of cells. The partial chemical substitution of the targeted elements can serve one of the following purposes: i) the effective suppression of the irreversible phase transition, ii) the significant promotion of the reversible phase transition, iii) the modulation of the phase transition process accompanied by the formation of new reversible phases, or iv) the simplification of the complex phase transition steps and suppression of phase transitions during discharging–charging. As summarized in Table 1, many elements (e.g., Mg, Co, Sn, Ti, Li, Cu, and Zn) have been used for the partial chemical substitution of the electrochemically active or inactive elements of P2- and O3-type electrodes to increase overall stability or reactivity. Most cathode materials present an average voltage range of 3.0–3.3 V (vs Na⁺/Na), a maximum optimized specific capacity of 190 mAh g⁻¹, and a remarkable capacity retention after cycling of ≈95% over 50–100 cycles.

Wang et al. have determined that the P2–O2 phase transition during cycling was inhibited via the partial substitution of Ni with Mg in a P2-type Na₀.₅M₀.₅Ni₀.₅O₂ electrode for Na storage.⁴⁰ Figure 3a–c illustrate that, unlike the major reflections of the Mg-free electrode, those of the initial P2 phase of the Mg-substituted electrode remained at 4.22 V, which indicated that no noticeable phase transitions occurred. Assisted by the immobile Mg²⁺ ions confined in the metal layers, more Na⁺ ions were moved to the prismatic sites during charging to stabilize the overall charge balance, and thus, the initial P2 structure was retained at high voltages. The high-angle annular dark field
Table 1. Summary of nano polymorphism strategies for improving the electrochemical performance of cathodes.

| Cathode material | Material synthesis method | Phase transition | Electrochemical performance$^{a}$ |
|------------------|---------------------------|-----------------|----------------------------------|
| Li[Ni$_x$Mn$_{1-x}$Co$_{0.2}$Ti$_{0.2}$O$_2$]$^{[1]}$ | Coprecipitation | $R3m$-layered phase to $Fm3m$ rocksalt | $AV = 2.7$ V, $RC = 210$ mAh g$^{-1}$, $CRR = 97\% (20)$ |
| 0.5Li$_2$Mn$_{0.5}$O$_3$·0.5Li$_4$Ni$_{0.44}$Mn$_{0.56}$O$_2$]$^{[14]}$ | Sol–gel reaction | Spinel and/or rocksalt | $AV = 2.8$ V, $RC = 218.3$ mAh g$^{-1}$, $CRR = 94.1\% (100)$ |
| O-deficient Li-rich Li$_{2}$Mn$O_3$$_{1.9}$Co$_{0.1}$O$_2$$_{0.1}$]$^{[15]}$ | Coprecipitation and gas–solid reaction | Activating Li and suppressing gas | $AV = 2.8$ V, $RC = 301$ mAh g$^{-1}$, $CRR > 93\% (150)$, $CE = 93.3\%$ |
| C-coated LiFePO$_4$ particles$^{[13]}$ | Ball milling and spray-pyrolysis | $Fe_{2}P$ phase | $RC = 125$ mAh g$^{-1}$, $CRR = 100\% (100)$ |
| Cu$_2$Fe$_{1.7}$P$_4$$^{[96]}$ | Ball milling | Reversible Cu redox ($Cu^{2+}$) reactions | $AV = 3.5$ V, $RC = 575$ mAh g$^{-1}$ |
| Mn-substituted P2-type | Solid-state reaction | Reversible | $P2$-OP4 |
| Cu$_{0.1}$Fe$_{0.9}$Mn$_{0.1}$O$_2$$_{0.9}$]$^{[14]}$ | Coprecipitation | O$_3$–P$_3$–O$_2$ | $AV = 2.9$ V, $RC = 190$ mAh g$^{-1}$, $CRR = 79\% (30)$ |
| Co-substituted O3-type | Solid-state reaction | Reversible | $P2$-OP4 |
| Na$_{2}$Fe$_{0.8}$Co$_{0.2}$O$_2$$_{0.8}$]$^{[13]}$ | Coprecipitation | O$_3$–P$_3$–O$_2$ | $AV = 3.3$ V, $RC = 160$ mAh g$^{-1}$ |
| Mg-substituted P2-type | Solid-state and solution reactions | Reversible | $P2$-OP4 |
| Na$_{2}$Li$_{0.6}$Mg$_{0.4}$O$_2$ ($0 \leq x \leq 0.2$)$^{[110]}$ | Solid-state reaction | Reversible | $P2$-OP4 |
| Mg-substituted P2-type | Solid-state reaction | Reversible | $P2$-OP4 |
| Na$_{2}$Li$_{0.4}$Ni$_{0.5}$Mg$_{0.5}$Mn$_{0.5}$O$_2$ ($x \leq 0.5$)$^{[13]}$ | Sol–gel reaction | Suppressing | $P2$–O2 |
| Mg-substituted P2-type | Solid-state reaction | Suppressing | $P2$–O2 |
| Na$_{2}$Li$_{0.4}$Mn$_{0.6}$Ni$_{0.4}$Mg$_{0.2}$ ($0 \leq x \leq 0.33$)$^{[90]}$ | Sol–gel reaction | Suppressing | $P2$–O2 |
| Sn-substituted O3-type | Solid-state reaction | Reversible | $O3$–P$_3$ |
| Na$_{2}$Ni$_{0.5}$Mn$_{0.5}$S$_{0.1}$O$_2$ ($y \leq 0.5$)$^{[128]}$ | Solid-state reaction | Reversible | $O3$–P$_3$ |
| Ti-substituted O3-type | Solid-state reaction | Reversible | $O3$–P$_3$ |
| Na$_{2}$Ni$_{0.5}$O$_{1.2}$Ti$_{0.8}$O$_2$ ($0 \leq x \leq 0.5$)$^{[119]}$ | Coprecipitation | Suppressing | $P2$–O2 |
| Li-substituted P2-type | Coprecipitation | Suppressing | $P2$–O2 |
| Na$_{2}$Li$_{0.4}$Ni$_{0.6}$Mg$_{0.2}$O$_2$ ($0 < x, y, z < 1$)$^{[140]}$ | Self- combustion reactions | Suppressing | $P2$–O2 |
| Li-substituted P2-type | Coprecipitation | O$_3$–O$_3$–P$_3$–P$_3$ | $AV = 3.1$ V, $RC = 180$ mAh g$^{-1}$, $CRR = 92.1\% (40)$ |
| Na$_{2}$Li$_{0.4}$Mn$_{0.6}$O$_2$$_{0.8}$ | Solid-state reaction | O$_3$–P$_3$–O$_3$–P$_3$ | $AV = 3.1$ V, $RC = 128$ mAh g$^{-1}$, $CRR = 85\% (100)$ |
| Li, Fe codoping O3-type | Ceramic method | O$_3$–P$_3$–O$_3$–P$_3$ | $AV = 3.1$ V, $RC = 100$ mAh g$^{-1}$, $CRR = 97\% (100)$ |
| Na$_{2}$Li$_{0.4}$Ni$_{0.6}$Mn$_{0.4}$S$_{0.2}$O$_2$$_{0.7}$ | Solid-state reaction | O$_3$–P$_3$–O$_3$–P$_3$ | $AV = 3.1$ V, $RC = 107$ mAh g$^{-1}$, $CRR = 78\% (200)$, $CE = 100\%$ |
| Mg-substituted O3-type | Solid-state reaction | O$_3$–P$_3$–O$_3$–P$_3$ | $AV = 3.1$ V, $RC = 100$ mAh g$^{-1}$, $CRR = 97\% (100)$ |
| Na$_{2}$Ni$_{0.5}$Mg$_{0.5}$S$_{0.2}$O$_2$ ($0 \leq x \leq 0.5$)$^{[148]}$ | Solid-state reaction | Free | $RC = 98$ mAh g$^{-1}$, $CRR = 94.2\% (128)$, $CE = 100\%$ |
| Low Na-content O3-type | Solid-state reaction | Free | $RC = 98$ mAh g$^{-1}$, $CRR = 94.2\% (128)$, $CE = 100\%$ |
| Cu-substituted P2-type | Solid-state reaction | Reversible | $P2$–OP4 |
| Na$_{2}$Li$_{0.4}$Cu$_{0.6}$Mn$_{0.2}$O$_2$ ($0 \leq x \leq 1/3$)$^{[110]}$ | Solid-state reaction | O$_3$–P$_3$ (no O$_3$–P$_3$) | $AV = 3.0$ V, $RC = 124$ mAh g$^{-1}$, $CRR = 70.2\% (500)$, $CE = 99\%$ |
| Cu, Ti-substituted O3-type | Solid-state reaction | Reversible | $P2$–O2 |
| Na$_{2}$Li$_{0.4}$Cu$_{0.6}$Mn$_{0.2}$Ti$_{0.2}$O$_2$$_{0.8}$ | Sol–gel reaction | Reversible | $P2$–O2 |
| Zn-substituted P2-type | Sol–gel reaction | Reversible | $P2$–O2 |
| Na$_{2}$Zn$_{0.5}$Ni$_{0.5}$Mn$_{0.2}$O$_2$ ($0 \leq x \leq 0.7$)$^{[151]}$ | Sol–gel reaction | Free | $AV = 2.9$ V, $RC = 147$ mAh g$^{-1}$, $CRR = 100\% (100)$ |
| O3-type NaNi$_{0.5}$Mg$_{0.5}$Co$_{0.2}$ | Sol–gel reaction | O$_3$–O$_3$–P$_3$–P$_3$ | $AV = 2.9$ V, $RC = 120$ mAh g$^{-1}$, $CRR = 100\% (50)$ |
| O3-type Na$_{2}$Ni$_{0.5}$S$_{0.2}$O$_2$$_{0.8}$ | Sol–gel reaction | O$_3$–P$_3$–O$_3$ | $AV = 3.0$ V, $RC = 117$ mAh g$^{-1}$, $CRR = 95\% (50)$ |
| P2/O3-type Na$_{2}$Li$_{0.6}$Ni$_{0.4}$Mn$_{0.2}$O$_2$$_{0.8}$ | Coprecipitation | P2/O3–P2/O3–P2/O3–P2/O3 | $AV = 3.0$ V, $RC = 125$ mAh g$^{-1}$, $CRR = 95\% (20)$ |
Table 1. Continued.

| Cathode material | Material synthesis method | Phase transition | Electrochemical performance\(^a\) |
|------------------|---------------------------|------------------|-----------------------------------|
| P2-type Na\(_{0.67}\)\(\{\text{Fe}_{0.5}\text{Mn}_{0.5}\}_{1-x}\text{Co}_x\)O\(_2\) \((0 \leq x \leq 0.2)\)\[^{[16]}\] | Solid-state reaction | P2–O2 | AV \(= 3.0 \text{ V, RC} = 190 \text{ mAh g}^{-1}, \text{CRR} = 60.5\% (60),\) CE \(= 98–99\%\) |
| P2-type K\(_x\)\(\{\text{Fe}_{0.5}\text{Mn}_{0.5}\}_{1-x}\text{Co}_x\)O\(_2\) \[^{[11]}\] | Solvent-thermal and annealing method | Reversible | P2–O2 | AV \(= 2.5 \text{ V, RC} = 151 \text{ mAh g}^{-1} (20 \text{ mAh g}^{-1}),\) CRR \(= 78\% (350)\) |
| P2-type K\(_{0.65}\)Fe\(_{0.5}\)Mn\(_{0.5}\)O\(_2\) \[^{[52]}\] | Solid-state reaction | Reversible | P2–O2 | RC \(= 125.5 \text{ mAh g}^{-1} (10 \text{ mAh g}^{-1}), \text{CRR} = 67\% (500)\) |
| P2-type K\(_{0.44}\)Ni\(_{0.22}\)Mn\(_{0.78}\)O\(_2\) \[^{[62]}\] | Conventional solid-state method | Reversible | P2–O2 | RC \(= 120 \text{ mAh g}^{-1} (0.5 \text{ C})\) |
| P2-type K\(_{0.44}\)Ni\(_{0.3}\)Fe\(_{0.3}\)O\(_2\) \[^{[63]}\] | Conventional solid-state method | Reversible | P2–O2 | RC \(= 120 \text{ mAh g}^{-1} (0.5 \text{ C})\) |
| β-MnO\(_2\) \[^{[84]}\] | Hydrothermal | Tunnelled β-MnO\(_2\) to layered Zn-buserite | RC \(= 225 \text{ mAh g}^{-1} (0.65 \text{ C}), \text{CRR} = 94\% (2000)\) |
| NaNi\(_{0.25}\)O\(_2\) nanobelts \[^{[55]}\] | Hydrothermal | NaNi\(_{0.25}\)O\(_2\) to Zn\(_2\)Ni\(_{0.5}\)O\(_3\) | RC \(= 281 \text{ mAh g}^{-1} (300 \text{ mAh g}^{-1}), \text{CRR} = 71\% (2000)\) |
| 2D layered V\(_2\)CT\(_x\) MXene \[^{[46]}\] | Pulsed electric current sintering and etching | V\(_2\)CT\(_x\) to V\(_2\)O\(_3\) | RC \(= 508 \text{ mAh g}^{-1} (200 \text{ mAh g}^{-1})\) |
| V\(_2\)O\(_5\) nanowires \[^{[129]}\] | Hydrothermal | Crystallized V\(_2\)O\(_5\) to amorphous Al\(_x\)V\(_2\)O\(_5\) | RC \(= 107 \text{ mAh g}^{-1} (10 \text{ mAh g}^{-1})\) |
| FeVO\(_4\) nanorods \[^{[127]}\] | Hydrothermal and dry annealing | FeVO\(_4\) to Al\(_x\)V\(_2\)O\(_4\) spinel | RC \(= 350 \text{ mAh g}^{-1} (60 \text{ mAh g}^{-1})\) |
| Al\(_x\)MnO\(_2\cdot n\)H\(_2\)O \[^{[128]}\] | In situ electrochemical transformation reaction | Spinel Mn\(_2\)O\(_3\) to amorphous and layered Al\(_x\)MnO\(_2\cdot n\)H\(_2\)O | RC \(= 467 \text{ mAh g}^{-1} (30 \text{ mAh g}^{-1}), \text{CRR} = 58.2\% (60)\) |

\(^a\)AV: average voltage; RC: reversible/maximum/optimized specific capacity; CRR: capacity retention ratio after cycling (cycle number); CE: coulombic efficiency.

Figure 3. Ex situ X-ray diffraction (XRD) patterns of the P2-type Na\(_{0.67}\)Mn\(_{0.33}\)Ni\(_{0.33}\)O\(_2\) electrode a) before and b) after Mg substitution (Na\(_{0.67}\)Mn\(_{0.67}\)Ni\(_{0.33}\)−\(x\)Mg\(_x\)O\(_2\), \(x = 0.05\)) at different discharge and charge states, which are highlighted by the dotted lines in the charge–discharge profiles in c). High-angle annular dark field scanning transmission electron micrographs of the d) P2-type Na\(_{0.67}\)Mn\(_{0.33}\)Ni\(_{0.33}\)−\(x\)Mg\(_x\)O\(_2\) \((x = 0)\) and e) Na\(_{0.67}\)Mn\(_{0.67}\)Ni\(_{0.33}\)−\(x\)Mg\(_x\)O\(_2\) \((x = 0.05)\) electrodes at a charging potential of 4.22 V. a–e) Reproduced with permission.\[^{[30]}\] Copyright 2016, Wiley-VCH. f) In situ XRD patterns of Cu-and-Ti-substituted O3-type Na\(_{0.45}\)Cu\(_{0.05}\)Mn\(_{0.45}\)Ti\(_{0.15}\)O\(_2\) during the initial charge and discharge step. Annular bright field scanning transmission electron micrographs of water-soaked g) Na\(_{0.15}\)Mn\(_{0.33}\)O\(_2\) and h) Cu-and-Ti-substituted O3-type Na\(_{0.45}\)Cu\(_{0.05}\)Mn\(_{0.45}\)Ti\(_{0.15}\)O\(_2\). f–h) Reproduced with permission.\[^{[41]}\] Copyright 2017, American Chemical Society. Here, P and O denote trigonal prismatic and octahedral phases, respectively.
(HAADF)-STEM images of the pristine and Mg-substituted P2-type Na0.67Mn0.33Ni0.13O2 electrodes (Figure 3d,e, respectively) further confirmed that after chemical substitution only the P2 phase was present during charging at 4.22 V. Owing to the effectively suppressed P2–O2 transition, the electrochemical properties of the Mg-substituted electrode were remarkably enhanced; the electrode presented a high reversible capacity of 123 mAh g$^{-1}$ and a maximum capacity retention of 92.4% after 100 cycles (17.3 mA g$^{-1}$). The chemical substitution strategy can also be used to suppress the unwanted phase transition process for O3-type cathode materials. An O3-type NaNi0.67Cu0.05Mn0.4Ti0.1O2 electrode material was produced by modifying the structure of NaNi0.35Mn0.65O2 via Cu and Ti substitution, and in situ XRD analysis revealed that a highly reversible O3–P3 phase transition occurred for the modified material without the appearance of monoclinic O’3 or P3 phases (Figure 3f).[41] In addition, the substitution could also benefit the inhibition of the spontaneous O3–P3 phase transition of the pristine electrode after aging experiments (Figure 3g,h), which indicated that substitution improved the air stability of the electrode. Consequently, compared to the pristine NaNi0.35Mn0.65O2 electrode, the NaNi0.45Cu0.05Mn0.4Ti0.1O2 electrode presented a smoother charge–discharge profile, a higher discharge capacity (124 mAh g$^{-1}$), and an excellent capacity retention (70.2% after 500 cycles).[42]

2.2.2. Sodiation Degree Control

Controlling the sodiation degree of cathode materials is another NPM strategy for improving the Na storage performance, particularly for Na-deficient P2-type layered oxide electrodes (Na0.67MoO2) with only 0.67 Na$^+$ ions in each formula unit. During half-cell measurements using metallic Na as the counter electrode, the P2-type cathodes with a high discharging capacity of ~200 mAh g$^{-1}$ can be fully converted to NaNMO2 upon cycling. However, in a full Na-ion system, the additional 0.33 Na$^+$ ions could not be compensated from its original structure during cycling, which caused a 30% decrease in the capacity of the Na0.67MO2 cathode. Furthermore, some Na$^+$ ions were deactivated and a solid electrolyte interface formed at the anode. Therefore, exploring Na-rich electrodes as effective reservoirs to compensate for the potential Na$^+$ loss is essential for achieving excellent reversibility. Zhang et al. have reported the presiodization of P2-Na0.67Fe2(PO4)F3 to form Na-rich P′2-2Na[Fe0.5Mn0.5]O2 and ‘Na0.33V2(PO4)F3’ phases. The energy storage densities of the full Na-ion batteries (SIBs) assembled using these Na-rich phases and C as the cathode and anode, respectively (C/P′2-2Na[Fe0.5Mn0.5]O2 and C/Na0.33V2(PO4)F3) were significantly higher (≥30%) than that of the C/Na0.67[Fe0.5Mn0.5]O2 SIB.[42]

When Na-rich Prussian blue analogues (e.g., NaNi0.4Cu1.3Fe(CN)$_6$·0.18H$_2$O, Na1.27Fe(CN)$_6$, Na1.17MnFe(CN)$_6$, Na1.27Fe(CN)$_6$, Na1.17MnFe(CN)$_6$, and Na0.53Fe(CN)$_6$·0.85H$_2$O) are used as SIB cathodes, they can deliver specific capacities in the range of 60–150 mAh g$^{-1}$. In addition, it was demonstrated that introducing an anionic redox process and promoting reversible oxygen redox reactions are favorable strategies for increasing the capacity of SIBs with Na-rich TMO electrodes. For example, depending on the O-related anionic redox activity, the Na3RuO4 cathode material delivered an initial charge capacity as high as 321 mAh g$^{-1}$.[43] Furthermore, by coupling the Na1.2Mn0.4Fe0.6O2 electrode with cationic with anionic contributions, it reversible O2$^-$ species were formed, which resulted in a high capacity of 179 mAh g$^{-1}$ upon charging to 4.4 V, and a good capacity retention of over 60% after 50 cycles.[46] Despite the favorable effect of anionic redox processes on capacity, they often cause significant structural damage during repeated Na uptake and release cycles, which is largely ascribed to the undesired metal migration and O loss.[47] Therefore, designing new stable cathode materials with suppressed structural degradation for high-performance SIBs is imperative.

2.3. NPM of K Cathodes

K-ion batteries (PIBs) are considered promising alternatives to LIBs and SIBs for large-scale energy storage systems.[48–51] This is largely attributed to the standard redox potential of K (−2.936 V vs SHE) being lower than that of Na (−2.714 V vs SHE), and similar to that of Li (−3.040 V vs SHE).[52–55] Therefore, the operating voltage of PIBs is higher than those of LIBs and SIBs, and that is supposed to contribute to the high energy density of PIBs. In addition, because K and Na (2.09 and 2.3 wt%, respectively) are more abundant than Li (0.0017 wt%) in the Earth’s crust, PIBs meet the sustainable development requirements for future large-scale energy storage systems.[56–59] In addition to being used for LIBs and SIBs, transition metal oxides are good candidates for PIBs, owing to their high theoretical capacities, good structural stability, low cost, and environmentally friendliness.[52,60] Typically, K,TMO2 compounds (TM = Mn, Fe, Co, Ni) present P- or O-type phases depending on the location of the K$^+$ sites.[61,62] However, because the ionic radius of K$^+$ (1.38 Å) is larger than that of Li$^+$ (0.76 Å), K$^+$ presents poor transport kinetics, which results in the power density of PIBs being lower than that of LIBs. Moreover, cathode materials typically undergo polymorphic changes upon K$^+$ intercalation and deintercalation, and severe side reactions with the electrolytes, which further cause capacity loss and affect cycling stability. Conversely, the reversible polymorphic change between the P- and O-type phases of K,TMO2 during charging and discharging can also deliver a high specific capacity and confer good cycling stability to cells.[61–63] Therefore, it is important to investigate P2- and P3-type transition metal oxides as PIB cathodes and unveil the potential of these oxides to increase the electrochemical performance of cells via phase engineering.

2.3.1. P2-Type Transition Metal Oxides

P2-type layered K,TMO2 cathode materials have been explored for high-performance PIBs by promoting their reversible polymorphic changes. Deng et al. synthesized P2-type K0.65Fe0.5Mn0.35O2 hierarchical microspheres using a solvothermal method followed by two-step calcination, as illustrated in Figure 4a. During the K$^+$ ion deintercalation process for PIBs, a polymorphic transition from hexagonal P2 to O2 phase occurred at 4.0 V, and subsequently the pure P2 phase reformed when
the battery was discharged at 1.6 V (Figure 4b). This demonstrated that the synthesized P2-type $K_{0.65}Fe_0.5Mn_0.5O_2$ electrode presented highly reversible polymorphism, which resulted in the excellent cycling stability of the PIB with a decrease in capacity of only 22% after 350th cycles. The full cell assembled using P2-type $K_{0.65}Fe_0.5Mn_0.5O_2$ and hard carbon as cathode and anode, respectively, presented an attractive cycling life of 100 cycles, and a capacity retention of over 80%. Other P2-type layered $K_xTMO_2$ cathode materials, such as $K_{0.64}Na_{0.04}[Ni_{1/3}Mn_{2/3}]O_2$, were also explored for PIBs by delaying the P2–O2 polymorphic transition.

Typically, P2-type $K_xTMO_2$ presents a low ion diffusion barrier with a good structural maintenance; however, the potential polymorphism during the irreversible transition to O2-type $K_xTMO_2$ could induce structural contraction and deteriorate battery performance. The main approaches to address this concern are boosting the reversibility of the P2–O2 transition and suppressing the underside phase transition via structural optimization and cell design.

2.3.2. P3-Type Layered Transition-Metal Oxide

In addition to P2-type $K_xTMO_2$ materials, P3-type layered $K_{0.5}MnO_2$ was explored as a promising cathode material for superior cycling performance during $K^+$ storage. As revealed using in situ XRD measurements, when $K_{0.5}MnO_2$ was used as PIB cathode, it underwent a highly reversible P3–O3–X polymorphic transition during charging and discharging in the voltage range of 1.7–4.5 V. The P3-type $K_{0.5}MnO_2$ electrode demonstrated a high specific capacity of $\approx 125$ mAh g$^{-1}$ at a current density of 10 mA g$^{-1}$ and a good cycle stability with a capacity retention of 67% over 500 cycles. The full cell assembled by pairing this cathode with a soft carbon anode presented an attractive capacity retention of 90% over 500 cycles.

Typically, P2-type $K_xTMO_2$ presents a low ion diffusion barrier with a good structural maintenance; however, the potential polymorphism during the irreversible transition to O2-type $K_xTMO_2$ could induce structural contraction and deteriorate battery performance. The main approaches to address this concern are boosting the reversibility of the P2–O2 transition and suppressing the underside phase transition via structural optimization and cell design.
range of 1.5–3.9 V (Figure 4c). Furthermore, theoretical calculations confirmed that the P3-type K,MnO₂ delivered the lowest formation energy at a high K content, whereas the O3-type framework was more stable at a low K content, which suggested a possible P3-to-O3 transition (Figure 4d). Moreover, the voltage profile of the cell also indicated that the P3–O3 transition progressed during the K⁺ intercalation and deintercalation processes (Figure 4e). Consequently, the P3-type K₀.₃MnO₂ electrode delivered a reversible specific capacity of ≈100 mAh g⁻¹.[61]

Developing suitable P3-type cathode materials that can effectively accommodate repeated K⁺ extractions and insertions and maintain structural integrity is challenging.[64] Recently, new types of P3-type materials, such as K₀.₆₉CrO₃,[65] K₀.₅[Mo₀.₈Fe₀.₂]Na₀.₁O₂,[66] and K₀.₅Co₀.₃Mn₀.₇O₂,[67] have been determined to present high-level polymorphism transitions without significant structural variations. These materials achieved a maximum reversible discharge capacity of ≈120 mAh g⁻¹ and displayed good capacity retention over 300–1000 cycles. To further meet the requirements of SIBs, more modulation solutions are needed for the structural optimization of P3-type TMO cathodes to suppress the rapid capacity fading during cycling. Furthermore, the polymorphism transformation mechanisms should be further investigated using in situ advanced techniques to offer new insights on material design and electrode optimization.

2.4. NPM of Zn Cathodes

Although SIBs and PIBs are considered to be promising alternatives to LIBs, they still present drawbacks, including relatively low energy density, high flammability, electrolyte stability, and safety concerns.[68,69] Therefore, recently, researchers have focused on exploring alternative low-cost, high-safety batteries with long cycle lives. Aqueous batteries based on multicharge carriers (Mg²⁺, Al³⁺, and Zn²⁺) are of particular interest because they can provide multiple electrons for redox reactions, and thus, present high specific capacities and energy densities.[70,71] Among them, rechargeable Zn-ion batteries (ZIBs) present great potential because Zn, the anode metal, is abundant and presents a low redox potential (~0.763 V vs SHE), with a high theoretical specific capacity (~820 mAh g⁻¹), and low toxicity.[72–77] Recently, many studies have been performed on high-performance ZIBs with metal Zn anodes and different types of cathode materials, such as Mn-based oxides,[78,79] V-based oxides,[80,81] and Prussian blue.[82]

2.4.1. Mn-Based Oxides

Among various ZIB cathode materials, Mn-based oxides, including MnO₂,[75,84] Mn₀.₉Na₀.₁O₂,[85] Mn₀.₇Na₀.₃O₂,[86] and MnNa₂O₂,[70] present relatively high theoretical capacities, adequate safety features, and low toxicity, are inexpensive, and require simple fabrication procedures. Zhang et al. reported a high-performance rechargeable Zn–MnO₂ battery with β-MnO₂, Zn, and Zn(CF₃SO₂)₂ with Mn(CF₃SO₂)₂ additive as the cathode, anode, and electrolyte, respectively (Figure 5a).[84] XRD and TEM analyses confirmed that the tunnel-structured MnO₂ polymorphs underwent phase transition to a new layered Zn-buserite phase during the first discharging step, followed by the reversible intercalation and deintercalation of Zn²⁺ cations. Consequently, the βMnO₂-based cell delivered the exceptional reversible capacities of 225 and 100 mAh g⁻¹ at the rates of 0.65 and 32.50 C, respectively (Figure 5b), which exceeded those of other Mn-based cathodes for aqueous ZIBs (Figure 5c).[84] Furthermore, the capacity retention of this cathode was as high as 94% for up to 2000 cycles at 6.50 C. The soft-packed Zn–MnO₂ battery exhibited a reversible capacity of 1550 mAh over 50 cycles and a high energy density of 75.2 Wh kg⁻¹.[84]

Despite the significant progress on Mn-based oxides for ZIBs, some major challenges still exist, as follows: i) nearly all Mn-based oxides undergo undesired polymorphism transitions, ii) a noticeable volume expansion is often observed during the repeated insertion and desorption of the active Zn²⁺ or H⁺ ions, iii) the poor electrical conductivity of Mn-based oxides negatively affects electron transfer, and iv) active species are lost owing to the dissolution of Mn in the electrolyte systems. To address these shortcomings, some effective strategies, including composite hybridization, defect and interlayer engineering, electrolyte optimization, and battery configuration designing,[88] have been proposed for improving the overall electrochemical performance of ZIBs.

2.4.2. V-Based Oxides

Compared to Mn-based oxides, V-based oxides (such as V₂O₅),[89,90] are promising cathode candidates for ZIBs owing to their low costs and open frameworks for hosting ions.[82,91] Among them, sodium vanadates, which primarily consist of V₂O₅ polyhedral layers, demonstrate good structural integrity when Na⁺ ions are inserted as pillars between layers, which is desirable for the reversible intercalation and deintercalation of Zn²⁺ in ZIBs.[92–94]

In 2018, Guo et al. explored the Zn²⁺ insertion and extraction behaviors of two typical sodium vanadates: Na₂V₅O₁₀-type layered structure (Na₃V₁₂O₃₂ and HNaV₆O₁₆·4H₂O) and βNa₀.₃V₁₂O₃₀₅-type tunneled structure (Na₆₀₉V₂O₁₉).[95] They determined that the structure of the Na₂V₅O₁₀-type layered sodium vanadates was destroyed after cycling, whereas that of the Na₆₀₉V₂O₁₉-type tunneled sodium vanadate did not collapse. However, the tunneled structure presented a low ion diffusion coefficient, and consequently, a low capacity (135 mAh g⁻³). Moreover, the electrochemical properties of the layered structure were better than those of the tunneled one, and the Na₆₀₉V₂O₁₉ cathode presented attractive cycle stability up to 2000 cycles. The ex situ HRTEM and SAED patterns illustrated in Figure 5d, revealed that the active Zn²⁺ ions were first inserted into the Na₆₀₉V₂O₁₉ layer upon discharging. This was accompanied by the formation of ZnₙNa₆₀₉V₂O₁₉ and appearance of ZnₙV₂O₅, a new phase. Subsequently, upon charging, most inserted Zn²⁺ ions could be extracted from the Zn-rich ZnₙNa₆₀₉V₂O₁₉ and ZnₙV₂O₅ compounds to produce a Zn-poor ZnₙNa₆₀₉V₂O₁₉ phase (n ≪ m) for the subsequent cycles.

2.4.3. MXenes

The capacity and cycling stability of ZIBs have been considerably improved using Mn- and V-based oxide as ZIB cathode materials. However, these ZIBs often present low voltage (below 1.0 V for
V-based nanostructures), which greatly limits their commercial applications.[96,97] MXenes are emerging 2D nanomaterials that have been widely used for energy storage applications.[98–100] Recently, Li et al. designed an aqueous Zn hybrid-ion battery (ZHIB) using a 2D layered V$_2$CT$_X$ MXene as the cathode, which was synthesized via wet chemical HF etching using V$_2$AlC MAX powder.[96] A new V$_2$O$_5$ phase was formed during the intercalation–deintercalation of the Li$^+$/Zn$^{2+}$ hybrid ions (Figure 5e), which could contribute to promoting the electrochemical performance of the ZHIB. This cell outperformed several ZIBs with Mn-, V-, and Prussian blue-based cathode materials and presented a capacity of over 500 mAh g$^{-1}$, an excellent energy density of over 380 Wh kg$^{-1}$ at 0.2 A g$^{-1}$, and an ultralong cycling life of over 18 000 cycles (Figure 5e,f).[96,98,101–104]

More studies have been conducted on the use of MXenes for LIBs and SIBs than on their use for ZIBs. However, conductive 2D MXene nanosheets with controllable surface are promising materials for future ZIB electrodes because of the following advantages.

i) The large MXene family with various polymorphisms by selective etching on MAX phases and rich functional groups by adjusting the synthesis conditions offers great potential for active ions storage. ii) MXene-assembled architectures can be rationally designed to promote desired polymorphisms. For example, 2D/2D heterostructures obtained by coupling 2D MXenes with other 2D species active toward Zn$^{2+}$ ions are expected to greatly improve the overall electrochemical performance of ZIBs. iii) The polymorphic transformation of MXenes to the corresponding oxide phases can further contribute to increasing the capacity of ZIBs. Therefore, it is expected that the optimal manipulation of the NPM of MXene materials will effectively improve the performance of ZIBs.

**2.5. NPM of Al Cathodes**

Al is the third most abundant element in the Earth’s crust. Rechargeable Al-ion batteries (AIBs) have drawn significant attention for their high theoretical capacity and low cost. However, the large Al atomic radius and large volume change during alloying–dealloying processes result in low cycle life and high polarization of AIBs. Recently, a new NPM approach has been proposed to improve the cycling performance of AIBs. This approach involves the use of MXenes as cathode materials for AIBs due to their unique structural characteristics and versatile properties.
attention because of their high gravimetric and volumetric capacities (2980 mAh g\(^{-1}\) and 8040 mA h cm\(^{-3}\), respectively).\(^{[105–110]}\) In addition, owing to the three-electron transfers process that occurs during the charging and discharging of AIBs, the specific capacities and energy densities of AIBs are higher than those of two-electron ZIBs and single-electron alkaline metal batteries, such as LIBs, SIBs, and PIBs.\(^{[111,112]}\) Recently, many researchers have devoted significant efforts to exploring suitable cathode materials, such as graphite,\(^{[113]}\) graphene,\(^{[114–116]}\) metal oxides (e.g., Co\(_3\)O\(_4\),\(^{[117]}\) V\(_2\)O\(_5\),\(^{[118]}\) CuO,\(^{[119]}\) and MoO\(_3\),\(^{[120]}\) metal sulfides (e.g., Co\(_9\)S\(_8\),\(^{[107]}\) VS\(_2\),\(^{[121]}\) CuS,\(^{[122]}\) SnS\(_2\),\(^{[123]}\) NiS,\(^{[124]}\) and MoS\(_2\),\(^{[125]}\) metal selenides (Cu\(_2\)Se,\(^{[126]}\) and FeVO\(_4\),\(^{[127]}\) which could improve the capability of the Al\(^{3+}\) and AlCl\(_4^-\) ions for fast intercalation and deintercalation. However, AIBs still present drawbacks, including cathode disintegration, sluggish reaction kinetics, insufficient cycling stability, and rapid capacity loss, which restrict their practical applications.\(^{[128]}\)

Gu et al. examined the reversible storage mechanism of V\(_2\)O\(_5\) nanowires for rechargeable AIBs.\(^{[129]}\) Particularly, after the intercalation of Al\(^{3+}\) ions during the first discharge step, a noticeable polymorphic change from crystallized V\(_2\)O\(_5\) nanowire (Figure 6a) to an amorphous Al\(_x\)V\(_2\)O\(_5\) metastable phase (Figure 6b) was identified at the edge of the nanowire. This polymorphic change was irreversible. Upon charging, a thick polymorphic transition interface was formed (Figure 6c), and this transition was reversible during the subsequent cycles, as illustrated in Figure 6d.\(^{[127,129]}\) Wu et al. synthesized a mixed-phase Al\(_x\)MnO\(_2\)·\(n\)H\(_2\)O cathode (Figure 6e) via an in situ electrochemical spinel-to-layered transformation reaction (Figure 6f,g) by introducing Al\(^{3+}\) and H\(_2\)O into spinel Mn\(_3\)O\(_4\) in a trivalent ion aqueous solution.\(^{[130]}\) The electrochemical performance of this AIBs, which delivered a high initial capacity of 467 mAh g\(^{-1}\) and retained over 270 mAh g\(^{-1}\) after 60 cycles, was remarkable (Figure 6h).

Despite various types of cathode materials being investigated for improving the electrochemical performance of AIBs, the development of AIB electrode materials is still in its infancy.\(^{[131–133]}\) The NPM of AIBs is mostly associated with the material types and electrolyte systems (e.g., organic solvents, ionic liquids, and aqueous and molten salts). Typically, the intercalation of AlCl\(_4^-\) anions and formation of C\(_6\)(AlCl\(_4^-\)) species...
during charging is the predominant reaction in carbonaceous electrode materials, and the intercalation of Al\(^{3+}\) cations accompanied by polymorphism changes often occurs in metal oxide/sulfide electrode materials. To alleviate the undesired irreversible transition processes on oxide or sulfide cathodes, the preferable structure should present large lattice and/or interlayer spacings to increase the Al\(^{3+}\) insertion–deintercalation rates. In future studies, more attention should be paid to the identification of potential cathode materials with desired structural features for the efficient intercalation of Al\(^{3+}\) and/or AlCl\(_4^-\) ions.

2.6. NPM of Air Cathodes in Metal–Air Batteries

Metal–air batteries include an air cathode, which facilitates the reduction of air into solid oxides upon discharging and the reverse process upon charging. Metal–O\(_2\) batteries in which O\(_2\) originating from the atmosphere air is used as the cathode are common metal–air batteries. Li–O\(_2\) and Na–O\(_2\) batteries have been the most studied metal–O\(_2\) batteries to date. An NPM change between O\(_2\) (gas) and O\(_{x}^-\) (condensed phase) often occurs at the cathodes of metal–O\(_2\) batteries during charging and discharging. This NPM change induces a large overpotential, and thus, leads to electrode surface passivation, which, subsequently, results in the limited capacity level, low energy efficiency, and poor cyclability of the batteries. Therefore, it is important to explore effective strategies for modulating the NPM changes, such as designing oxygen anion-redox cathodes in which no gaseous O\(_2\) evolves, to boost the electrochemical performance of metal–O\(_2\) batteries.

2.6.1. Li–O\(_2\) Batteries

The theoretical gravimetric energy density of aprotic Li–O\(_2\) batteries was calculated to be 3458 Wh kg\(^{-1}\), based on the formation of insulating lithium peroxide (2 Li + O\(_2\) \rightarrow Li\(_2\)O\(_2\)) at an equilibrium potential of 2.96 V.[157] To activate a Li–O\(_2\) battery, the phase change between gaseous O\(_2\) and condensed O\(_{x}^-\) is required to occur at the cathode, initially. This creates a 10\(^4\)-fold volume difference, and thus, an extremely high overpotential, particularly during charging (>0.1 V upon discharging and >1.1 V upon charging). Consequently, a low round-trip efficiency and significant decrease in capacity have always been reported for Li–O\(_2\) batteries. Zhu et al. designed an oxygen anion-redox cathode in which no gas evolved by confining amorphous nanolithia into a cobalt oxide catalytic skeleton, as illustrated in Figure 7a.[158] This cathode presented a gravimetric capacity of \(\approx 1000\) Wh kg\(^{-1}\) based on the weight of the entire composite and a discharge capacity of 587 Ah kg\(^{-1}\) at 2.55 V. Furthermore, the cell in which this cathode was paired with a Li\(_4\)Ti\(_5\)O\(_12\) anode presented excellent stability as its capacity decreased by only 1.8% after 130 cycles. Moreover, the round-trip overpotential of the cell significantly decreased to 0.24 V, and the unique self-protective mechanism from O\(_2\) gas release and overcharging was achieved via the automatic shuttling of the self-generated radical species (A/A\(_{x}^-\)) soluble in the electrolyte systems, as illustrated in detail in Figure 7b,c. An intermediate peroxide radical (A), which was initially formed via the ring opening reaction with the solvated O\(_2^-\) attacked the methylene group of the ethylene carbonate solvent, diffused to the anode side and accepted electrons to form A\(_{x}^-\) ions, which, in turn, diffused back to the cathode side. Depending on the A/A\(_{x}^-\) redox cycle, a shunting current was achieved through the electrolyte system.[158]

Other effective NPM engineering strategies have been reported for alleviating the high charge polarization and promoting the stability of Li–O\(_2\) batteries. For example, the introduction of suitable redox mediators is favorable for decreasing undesired charge polarization behaviors.[159] Specifically, in
the presence of O₂ evolution redox mediators, the charge potential can be substituted by the potential of a redox mediator couple, in which the mediators often prefer to lose electrons upon charging and the oxidized mediators can further react with Li₂O₂ to recover to the initial form. To date, a wide range of redox mediators, including organic (e.g., tetrathiafulvalene, 2,2,6,6-tetramethyl-1-piperidinyloxy), inorganic (e.g., LiNO₃), and biological materials (e.g., metal phthalocyanines and porphyrin), have been studied for addressing these aspects during the oxygen evolution and oxygen reduction reactions (OER and ORR, respectively) in Li–O₂ batteries. Typically, redox mediators for the OER decrease the charge potential, hinder the undesired side reactions, and increase the round-trip efficiency of the Li–O₂ batteries. Conversely, redox mediators for the ORR can effectively improve the discharge capacity and reduce the electrolyte decomposition and degree of electrode corrosion. If dual redox mediators are used for the discharge and charge processes, their synergistic effects can significantly improve the overall electrochemical performance of Li–O₂ batteries. These redox mediators are mainly active for the primary product (Li₂O₂), and it is expected that promising practical mediators should also be active for some common by-products in Li–O₂ systems, such as Li₂CO₃ and LiOH. Recently, 2,5-di-tert-butyl-1,4-dimethoxybenzene, an effective trifunctional redox mediator for Li–O₂ batteries, has been demonstrated to be capable of capturing Li⁺ and reactive O₂⁻ species. This reduced the undesired parasitic reactions toward the solvent, increased the Li₂O₂ yield up to 96.6%, and removed the Li₂CO₃ and LiOH byproducts.

2.6.2. Na–O₂ Batteries

For Na–O₂ batteries, an extremely low overpotential of less than 0.2 V is required for the oxidation of the micrometer-sized sodium superoxide (NaO₂) product during charging despite the low theoretical capacity (≈1100 kWh kg⁻¹) of these batteries. This indicated that Na–O₂ batteries presented better reversibility than Li–O₂ batteries. However, previous studies have identified different types of discharge products, including sodium peroxide (Na₂O₂), sodium hydroxide (NaOH), and sodium carbonate (Na₂CO₃), but not NaO₂. Despite the progress in Na–O₂ battery research, the underlying formation mechanisms of NaO₂ as the primary discharge product have not been elucidated yet. To confirm the nucleation and growth mechanism of the main discharge product of Na–O₂ batteries, operando electrochemical TEM measurements and a liquid aprotic electrolyte were used to investigate the structural phase evolution of NaO₂ during discharging. NaO₂ cubes were formed from small NaO₂ nuclei via a solution-mediated nucleation process, and subsequently, the crystals grew isotropically. An outer organic–inorganic shell was formed at the NaO₂/electrolyte interface during the potential parasitic reactions between the growing product and electrolyte molecules, which was believed to contribute to the poor cycling stability of Na–O₂ batteries. Upon charging, the NaO₂ cubes were gradually dissolved but parts of the shell remained and spread on the electrode surface at the end of the charging process. To evaluate the stability of the discharge product (NaO₂), a built-in solid-state Na–O₂ nanobattery comprising...
a metal Na metal anode, carbon nanotube (CNT) cathode, and Na₂O solid electrolyte was subjected to in situ environmental TEM analysis (Figure 8d). After 8 h of staging under vacuum, the major phase of the large NaO₂ cubic particles maintained the original Pm3m structure, and a small amount of Pnmm phase was also formed (Figure 8e,f). Conversely, no change was observed in the structure of the conformal coatings on the CNTs (NaO₂ + Na₂O₃) (Figure 8g,h), which suggested that NaO₂ presented excellent intrinsic stability in the system in which NaO₂ did not come in direct contact with the liquid electrolyte. It can be inferred that solid electrolytes favor the stabilization of the discharge product (NaO₂) and the complex side reactions with the liquid electrolyte in liquid Na–O₂ batteries can be effectively avoided using solid-state cells.

2.6.3. Other Metal–Air Batteries

Unlike the main discharge products of Li–O₂ and Na–O₂ batteries, that of K–O₂ batteries is the kinetically and thermodynamically stable KO₂, which confers a unique feature to nonaqueous K–O₂ batteries. Compared to Li–O₂, Na–O₂, and K–O₂ batteries, Zn–O₂ batteries present great potential for practical applications, mostly owing to the low cost and good stability of Zn in aqueous electrolytes. Different types of cathode catalysts with excellent OER and ORR activities have been explored for rechargeable Zn–O₂ batteries. In addition, other types of metal–oxygen batteries (e.g., Mg–O₂ and Al–O₂ batteries) and some emerging metal–air batteries (e.g., Li-N₂, Li-CO₂, Na-CO₂, K-CO₂, Zn-CO₂, and Al-CO₂) batteries have been reported in the literature.

Among these metal–air batteries, Li–CO₂ batteries have received significant attention because they reuse CO₂ as a renewable energy carrier and reduce the anthropogenic CO₂ emissions. To date, a wide range of electrocatalysts, such as noble metal nanoparticles, metal–organic frameworks, covalent organic frameworks, metal oxides, metal carbides, metal phosphides, graphene/CNTs/carbon, metal polyphthalocyanines, and metal/carbon hybrids have been investigated for activating stabilized CO₂, manipulating the discharge product distribution, and promoting reversibility in Li–CO₂ batteries. The main discharge products of the reduction process in Li–CO₂ batteries include Li₂CO₃ and carbon. Upon charging, Li₂CO₃ can be easily decomposed; however, the efficient decomposition of the produced carbon specie seems challenging. In 2017, Qiao et al. designed an aprotic Li–CO₂ battery with completely reversible Li–CO₂ electrochemistry, in which both Li₂CO₃ and carbon decomposed in the presence of a Ru catalyst and the effective CO₂ fixation was achieved via an electrochemical reduction process (Figure 9a). Previous studies confirmed...
that Ru catalysts promoted the reversible transformations of Li$_2$CO$_3$ and carbon and inhibited the undesired electrolyte decomposition reactions.$^{[212]}$ In the absence of catalysts, the reversible cycle cannot be recycled owing to the irreversibility of the resultant carbon; moreover, upon charging, the as-produced superoxide radicals induce severe electrolyte decomposition reactions, which reduce the electrochemical performance of the battery (Figure 9b)$^{[213]}$. The Li–CO$_2$ battery featuring a Super P carbon loaded with Ru nanoparticles as the cathode, could be operated for 80 cycles and presented a cut-off capacity of 1000 mA h g$^{-1}$ at a current density of 100 mA g$^{-1}$.$^{[212]}$

For the current Li–CO$_2$ battery systems, cathode passivation and large overpotentials are frequently reported, and are attributed to the insoluble and nonconductive Li$_2$CO$_3$ discharge product. The introduction of a trace amount of O$_2$ into Li–CO$_2$ batteries has been demonstrated to dramatically improve their electrochemical properties.$^{[214]}$ When the underlying formation mechanism of Li$_2$CO$_3$ was analyzed (Figure 9c), it was revealed that, in high-donor-number (DN) solvents, Li$_2$CO$_3$ was formed via an “electrochemical solution method” and a peroxodicarbonate (C$_2$O$_6^{2-}$) intermediate was also produced. Conversely, in low-DN solvents, Li$_2$CO$_3$ was formed when Li$_2$O$_2$ and CO$_2$ reacted via a “chemical surface method.”$^{[215]}$ Furthermore, O$_2$ could act as a “pseudocatalyst” to activate CO$_2$ in high-DN systems but not in low-DN electrolytes upon discharging. This mechanistic study offered guidance for improving the performance of Li–CO$_2$ batteries by optimizing the electrolyte system design.

2.7. NPM of S Cathodes in Metal–Sulfur Batteries

Owing to its remarkable theoretical capacity for Li storage ($\approx$1675 mA h g$^{-1}$) and abundance, S is an appealing cathode material compared to the common LIB and SIB cathode materials.$^{[216–218]}$ For Li–S batteries, upon discharging, solid S is converted to Li$_2$S$_2$ ($S_8 + 8$ Li $\rightarrow 4$ Li$_2$S$_2$) and Li$_2$S ($S_8 + 16$ Li $\rightarrow 8$ Li,S), which are reversibly converted into solid S during charging. However, some polysulfide intermediates (e.g., Li$_2$S$_4$, Li$_2$S$_6$, and Li$_2$S$_8$), which are easily soluble in electrolyte systems, always form during the reversible transitions between S and insoluble Li$_x$S species.$^{[5,219]}$ As illustrated in Figure 10a, this leads to the unwanted shuttle effect accompanied by the uncontrolled deposition and loss of S-based active species, which has been considered the primary reason for Li–S battery failures in terms of coulombic efficiency and specific capacity.$^{[220–224]}$ Owing to the solubility of polysulfides in electrolytes, the direct observation of these species is a major challenge. Until 2017,
operando XRD measurements have revealed the distinct XRD signature of long-chain polysulfides, which are adsorbed at the surface of glass fibers during lithiation and delithiation (Figure 10b).[225]

The effective strategies have been proposed to address the shuttle effect, to date, can be summarized as follows: i) encapsulating the soluble Li$_x$S species into targeted matrices (e.g., carbon, graphene, oxides, sulfides, polymers, and metals),[226–231] ii) trapping the soluble Li$_x$S species using bifunctional binders based on the opposite bonding nature of nonpolar S and polar Li$_x$S species,[212,213] iii) controlling the deposition states of Li$_x$S species using hydrophilic electrode surfaces,[220] iv) replacing S with lithium sulfides (e.g., Li$_2$S) as the starting cathode material to avoid the expansion of S,[234,235] v) modifying the separator to change the migration pathway of polysulfides,[236] and vi) suppressing the polysulfide shuttle using additional electrolyte additives (e.g., P$_2$S$_5$) or surface redox reactions.[237,238]

Recently, Pan et al. have developed a nonencapsulation approach that involved the controlled nucleation and growth of S species using a low-surface-area carbon fiber architecture for high-performance Li–S batteries.[239] Figure 10c,d illustrate the major differences between this novel approach and the traditional encapsulation strategies using high-surface-area carbon. The traditional melt-diffusion encapsulation methods often bring about a continuous uneven insulating S/Li$_2$S film after cycling (Figure 10e,f). However, the proposed electrochemical precipitation process promoted the heterogeneous nucleation and growth of S species accompanied by the formation of microsized “flower-like” S/Li$_2$S particles on the conductive network (Figure 10g,h). By manipulating the phase morphology, large open S-related-related spheres were formed on the carbon surface and no undesired insulating films were produced, which greatly boosted the S utilization efficiency (>100%) and thus, contributed to the outstanding coulombic efficiency (>99%) and high energy density (1835 Wh kg$^{-1}$ and 2317 Wh L$^{-1}$) of the batteries.[239]

3. NPM of Oxidation Electrodes

3.1. Typical Li Anodes

Si, one of the most promising candidate for replacing the commonly used graphite as high-specific-capacity anode material, is abundant in nature and presents a remarkable theoretical capacity that can reach 4200 mAh g$^{-1}$ and a suitable operating voltage of ~0.3 V (vs Li/Li$^+$). Many studies on Si anodes have revealed that Si transforms into amorphous Li$_x$Si, which subsequently transforms into crystalline compounds (e.g., Li$_{15}$Si$_4$ and Li$_{22}$Si$_5$) upon lithiation.[241–243] Density functional theory calculations (Figure 11a–d) confirmed that the formation energies of crystalline alloys were lower than those of amorphous ones (Figure 11a) and crystalline Li$_{15}$Si$_4$ formed under the largest driving force (Figure 11b).[242] Moreover, a significant volume expansion (>300%) occurred during the latter phase transition of the Si anodes, and led to the decrease in stability during cycling. Coating conductive layers onto Si anodes has been demonstrated to be an effective solutions for overcoming these issues. When the surface-protective layer is introduced, the formation of the final crystalline compound is expected to

![Figure 11](https://example.com/fig11.png)

Figure 11. a) Calculated formation energy of crystalline and amorphous Li$_x$Si and b) the driving force ($\Delta G = G_{cry} - G_{amo}$) is the difference between the Gibbs free energies of the crystalline (cry) and amorphous (amo) phases for the crystallization process as a function of the number of Li atoms per Si atom ($x$). c,d) Atomic structure models of amorphous (Li$_x$Si, $x = 3.75$) and crystalline (Li$_{15}$Si$_4$) structures. a–d) Reproduced with permission.[242] Copyright 2012, American Chemical Society. Filtered high-resolution transmission electron micrographs of the e,f) lithiated Fe$_3$O$_4$ phase formed during in situ lithiation at $\approx 150$ mA g$^{-1}$ and g) partially lithiated Fe$_3$O$_4$ phase formed during ex situ lithiation at 92.6 mA g$^{-1}$, illustrating the rocksalt (green) and spinel (red) phases. The insets in (e) and (f) are the fast Fourier transform (FFT) patterns of the rocksalt (green) and spinel (red) phases. h) FFT pattern of the region from (g). e–h) Reproduced under the terms of the CC-BY 4.0 license.[254] Copyright 2016, The Authors, Springer Nature.
be partly restrained, and the unwanted side reactions between Si and the electrolyte systems can be partly mitigated. Moreover, the surface modified with conductive layers coating confines the volume expansion and maintains a good electrical contact for promoting the ion–electron transfer processes.\textsuperscript{[244,245]}

Compared to metal oxide cathode materials, TMOs have attracted considerable interests as potential anode candidates for LIBs.\textsuperscript{[246]} Different types of TMOs with different morphologies and structures have been successfully synthesized and their electrochemical behaviors have been well-studied. However, the underlying phase conversion pathways, such as the nucleation and growth mechanisms, remain a major challenge for further in-depth investigations on battery technologies despite the recently achieved progress.\textsuperscript{[247]} In brief, there are two primary and common types of Li\textsuperscript{+} storage mechanisms, namely alloying-type (M\textsubscript{2}O\textsubscript{y} + 2y Li\textsuperscript{+} + 2y e\textsuperscript{−} ⇔ xM + y Li\textsubscript{2}O; M + z Li\textsuperscript{+} + z e\textsuperscript{−} ⇔ Li\textsubscript{z}M, e.g., SnO\textsubscript{2} and conversion-type (M\textsubscript{2}O\textsubscript{y} + 2y Li\textsuperscript{+} + 2y e\textsuperscript{−} ⇔ xM + yLi\textsubscript{2}O, e.g., Co\textsubscript{3}O\textsubscript{4}, Fe\textsubscript{2}O\textsubscript{3}, Mn\textsubscript{3}O\textsubscript{4}).\textsuperscript{[248–253]} Among TMOs, spinel TMOs are believed to be promising anode materials based on the two-step reaction during the equilibrium lithiation process, in which intercalation and conversion occur sequentially, from the viewpoint of chemical thermodynamics. However, the HRTEM images obtained during the in situ and ex situ Li intercalation, which explicitly visualized magnetite (Fe\textsubscript{3}O\textsubscript{4}) spinel, confirmed that the initial Li intercalation process, in which the rocksalt LiFe\textsubscript{3}O\textsubscript{4} phase was formed (Figure 11e–h) significantly overlapped with the subsequent conversion reaction, and that indicated that the reaction kinetics played a crucial role during lithiation.\textsuperscript{[254]}

In addition, size-dependent redox mechanisms have been commonly reported for solid oxide electrodes. For example, a two-phase transformation process is always involved for bulk Ti-containing (e.g., Li\textsubscript{2}Ti\textsubscript{5}O\textsubscript{12} and TiO\textsubscript{2}) electrodes. However, this changes to a single-phase solid-solution behavior when the particle size is greatly decreased, typically to less than 5 nm.\textsuperscript{[255,256]} Moreover, the trapped water content of these oxide anode materials has been confirmed to affect their overall electrochemical properties. Multiphase lithium titanate hydrates, which present single solid-solution behavior during cycling, as revealed using in situ synchrotron diffraction, presented a high specific capacity of ≈130 mA h g\textsuperscript{−1} at a rate of ≈35 C. Moreover, these electrodes can sustain more than 10 000 cycles, and their capacity only decreases by 0.001% per cycle.\textsuperscript{[257]}

### 3.2. Typical Na Anodes

In contrast to the numerous LIB anode materials, only a few promising NIB anode materials have been reported.\textsuperscript{[19,258]} Among them, hard carbon (HC) and Na\textsubscript{2}Ti\textsubscript{5}O\textsubscript{12} (NTO), which present relatively high capacity and stability, are the most common. However, the Na storage voltages of these electrode materials are relatively low (≈0 and 0.2 V vs Na\textsuperscript{+}/Na for HC and NTO, respectively), which leads to the potential deposition of metallic Na on them and causes significant safety concerns.\textsuperscript{[259,260]}

Spinel Li\textsubscript{2}Ti\textsubscript{5}O\textsubscript{12}, as a promising “zero-strain” anode material for high-performance LIBs, has been investigated as anode material for room-temperature SIBs. When combined with suitable binders, the Li\textsubscript{2}Ti\textsubscript{5}O\textsubscript{12} anode demonstrated a stable specific capacity of 155 mA h g\textsuperscript{−1} and coulombic efficiency of over 99%. Using in situ synchrotron XRD and advanced STEM results, a reversible three-phase separation storage mechanism was proposed for the Li\textsubscript{2}Ti\textsubscript{5}O\textsubscript{12} anode in 2013.\textsuperscript{[261]} As Na\textsuperscript{+} ions are progressively inserted into the Li\textsubscript{2}Ti\textsubscript{5}O\textsubscript{12} anode, they occupy the 16c vacant sites and Li\textsuperscript{+} ions are simultaneously transferred from the initial 8a sites to the 16c sites owing to coulombic repulsions. This results in the formation of the V\textsuperscript{8b}[Li\textsubscript{6}Na\textsubscript{6−x}]\textsuperscript{x}[Li\textsubscript{16}Ti\textsubscript{5}O\textsubscript{12}] intermediate which is further separated into the V\textsuperscript{8b}[Na\textsubscript{6}]\textsuperscript{3}[Li\textsubscript{16}Ti\textsubscript{5}O\textsubscript{12}] and V\textsuperscript{8b}[Li\textsubscript{6}][Li\textsubscript{16}Ti\textsubscript{5}O\textsubscript{12}] rocksalt phases owing to the different sizes of the Li\textsuperscript{+} and Na\textsuperscript{+} guest ions.

Transition metal dichalcogenides, which have been widely studied as electrocatalysts, have also been explored as potential electrode materials for rechargeable batteries.\textsuperscript{[262]} During the intercalation of Li\textsuperscript{+}, the MoS\textsubscript{2} electrode often undergoes transition between the semiconducting 2H and metallic 1T/1T′ phases.\textsuperscript{[263–265]} It is hypothesized that this phase transition may also occur during the intercalation of Na\textsuperscript{+}. In situ HRTEM was used to track the real-time structural evolution of MoS\textsubscript{2} during intercalation, and the results revealed that the two-phase reaction mechanism for Na\textsuperscript{+} insertion was initiated by the nucleation of NaMoS\textsubscript{2}, a new phase, followed by the propagation of the NaMoS\textsubscript{2}/MoS\textsubscript{2} phase boundary with a typical width of ≈2 nm (Figure 12a) and a much lower propagation rate (≈3–7 nm s\textsuperscript{−1}) than the Li\textsuperscript{+} diffusion rate. Moreover, the 2H-MoS\textsubscript{2} phase was converted to a superstructured 1T-NaMoS\textsubscript{2} phase as the intercalation proceeded.\textsuperscript{[266]} The phase transition process may not always be the same during the intercalation of different types of ions. Recently, manganese sulfide (MnS\textsubscript{2}), which transitioned from the α to the β phase (Figure 12b) during the first cycle, was demonstrated to improve the Li\textsuperscript{+}-storage performance of a MnS\textsubscript{2}-based anode that consisted of MnS nanoparticles in situ encapsulated into N,S-doped nanotube-like carbon (Figure 12c). The anode material presented a remarkable capacity (1415 mA h g\textsuperscript{−1} at 0.05 A g\textsuperscript{−1}) and long-term stable cycling over 5000 cycles. However, when this anode was used for Na\textsuperscript{+} intercalation, no such phase transition occurred during the initial sodiation–desodiation process, as confirmed using ex situ XRD experiments. Nevertheless, this anode presented a much higher rate capacity than the bulk α-MnS anode (Figure 12d) and a negligible capacity decay of 0.09% per cycle after 200 cycles (Figure 12e).\textsuperscript{[267]}

In addition, some other alloy-type materials, including red P and Bi have been considered to be promising anode materials for high-performance SIBs.\textsuperscript{[268]} The theoretical specific capacity of elemental P is as high as 2596 mA h g\textsuperscript{−1} owing to the three-electron reaction that leads to the formation of Na\textsubscript{3}P and relatively low operating potential of ≈0.45 V.\textsuperscript{[269]} Conversely, compared to flammable white P and high-cost black P, red P is commercially available and cost-effective.\textsuperscript{[270,271]} A recent study has revealed that sodiation confers red P particles a “liquid-like” behavior and the sodiation-induced softening polymorphism transformation can contribute to improving the mechanical malleability and deformability against pulverization in SIBs.\textsuperscript{[272]} The major challenges for the wide utilization of red P for practical SIBs are the low intrinsic electrical conductivity of P (≈10\textsuperscript{−14}–10\textsuperscript{−12} S cm\textsuperscript{−1}), sluggish reaction kinetics, and extremely large volume expansion (≈300–500%).\textsuperscript{[273]}
To address these drawbacks, several strategies have been proposed, such as hybridization with a conductive matrix (e.g., carbon,[274] hierarchical porous carbon,[275–278] 3D carbon frameworks,[279] N-doped carbon nanofibers,[280] N-doped microporous carbon,[281] polypyrrole,[282] polycrilonitrile,[283] carbon nanotubes,[284,285] and graphene,[286–290]) and nanostructure engineering (e.g., hollow nanospheres[291] and core–shell structures[292]). Although red P–carbon composites have been extensively investigated owing to their simple fabrication technology and affordability, the practical requirements of SIBs have still not been met yet. Most red P–carbon composites contain a high percentage of carbon (>30 wt%), which leads to a low tap density and relatively low capacity.[293] Hence, improving the utilization ratio of the high-capacity red P component and exploring the specific polymorphism transition processes remain important research directions for future studies.

Compared to red P, metallic Bi presents a small volumetric expansion ratio of ≈250%; moreover its gravimetric and volumetric capacities are ≈390 mAh g⁻¹ and ≈3800 mAh cm⁻³, respectively.[294,295] Operando XRD experiments revealed that a two-step alloying process occurs during sodiation upon discharging. That led to the appearance of two voltage plateaus, which were accompanied by the formation of two polymorphic phases: NaBi and Na₃Bi. Upon charging for desodiation, a reversible dealloying process was identified, in which a gradual polymorphic transformation from Na₃Bi to NaBi, and lastly Bi occurred.[296,297] However, other studies indicated that the polymorphism transition upon sodiation was largely associated with the initial Bi grain size.[298] Further in situ TEM observations of ultrathin Bi nanosheets confirmed the occurrence of a multistep Bi → NaBi → c-Na₃Bi → h-Na₃Bi (hexagonal) polymorph transformation process from during alloying.[299] To improve the performance of Bi anodes for SIBs, many optimization approaches, such as nanosize engineering,[300] bimetallic alloying,[301–303] hybridization with carbonaceous materials,[304–309] and electrolyte optimization,[310] were developed to meet the practical requirements for SIBs. Despite the significant progress in the use of Bi-based anodes for SIBs, more efforts should be dedicated to the synthesis technology development, chemical component optimization, and electrode configuration design improvement to overcome the unsatisfactory coulombic efficiency and cycling stability of these SIBs.

3.3. Typical K Anodes

Carbon-based materials, such as graphite,[311,312] hard and soft carbon,[313] and graphene,[312] present good electrical conductivity and excellent safety and are inexpensive. When used as PIB anodes, these materials facilitate K⁺ ion intercalation and can deliver a theoretical specific capacities of ≈273 mAh g⁻¹.[314–317] However, their limited capacity and rapid capacity fading cannot meet the demands for the practical PIB applications. Therefore, it is imperative to continue to research and develop advanced PIB anode materials with high electrochemical K⁺ storage capacity.[68] Metal chalcogenides, including metal sulfides and selenides, which have been widely investigated as LIB and SIB electrodes owing to their remarkable theoretical
capacities and excellent redox reversibility, are considered to be promising PIB materials. The M–X bonds in chalcogenides are weaker than the M–O bonds in metal oxides owing to the atomic radii of chalcogens being larger than that of O. This could facilitate fast ion migration and lower the energy barrier of the intercalation–deintercalation reactions. However, a major drawback of PIB anodes is the large volume variation during cycling, which could lead to undesired electrode pulverization and, consequently, poor cycling stability.

In terms of underlying mechanisms, typically, both intercalation and conversion reactions occur during potassiation, and the full conversion can damage the layered structure and, consequently, lead to rapid capacity fading. Du et al. have recently revealed the phase competition reactions between intercalation and conversion in microsized MoS$_2$ for PIBs, which presented a rate-dependent behavior and excellent cyclic stability. Specifically, as illustrated in Figure 13a, when the MoS$_2$ electrode was cycled at a low rate...
of 50 mA g\(^{-1}\), \(K_{1.0}\MoS_2\) was converted to \(K\MoS_2\). If the rate was increased to 500 mA g\(^{-1}\), full intercalation was achieved accompanied by the formation of \(K_0.2\MoS_2\) and \(K_0.3\MoS_2\), which were partly recovered to \(\MoS_2\) during the subsequent charging step. If the rate was further increased to 1000 mA g\(^{-1}\), the intercalated \(K_0.4\MoS_2\) compound was identified at 0 V, which was almost fully recovered to \(\MoS_2\) during the subsequent charging step. Furthermore, the intercalation and conversion capacity contribution ratios were roughly evaluated based on the reversible and theoretical capacities, and the results confirmed that the intercalation capacity contribution ratios exceeded 60% at 1000 mA g\(^{-1}\) and were lower than 30% at 50 mA g\(^{-1}\) (Figure 13a). This large contribution difference at different rates was attributed to the relatively faster kinetics of the intercalation reaction compared to that of the conversion reaction. Conversely, a polymorphic change from the initial 2H-\MoS_2 phase to the 1T-\(K_1.0\MoS_2\) phase occurred during \(K^+\) ion insertion, which has also been commonly observed during the intercalation of \(\text{Li}^+\) and \(\text{Na}^+\) ions.\(^{264,266}\) This transition was accompanied by the increase in \(d\)-spacing from 6.1 Å for \(\MoS_2\) to 79 Å for \(K_0.3\MoS_2\) after the first discharge step. This larger interlayer spacing was beneficial for promoting the ion diffusion kinetics and buffering the volume expansion during \(K^+\) intercalation reactions, and hence, improved the cycling stability of PIBs.\(^{1329}\)

Ge et al. reported another layered PIB anode that achieved efficient \(K^+\) ion diffusion via expanding the interlayer spacing. They synthesized a spherical \(\text{MoSe}_2/\text{N-doped carbon composite featuring numerous carbon-coated MoSe}_2\) nanosheets with a large interlayer spacing of 0.68 nm using a solvothermal reaction in the presence of ethylenediamine and glucose (Figure 13b).\(^{329}\) This \(\text{MoSe}_2\)-based electrode presented excellent rate performance and cycling stability for electrochemical \(K\) storage. Its reversible capacity exceeded 250 mAh g\(^{-1}\) over 300 cycles at 100 mA g\(^{-1}\), and was \(\approx 200\) mAh g\(^{-1}\) at 1000 mA g\(^{-1}\) and \(\approx 180\) mAh g\(^{-1}\) at 2000 mA g\(^{-1}\) (Figure 13b). The ex situ XRD and Raman analyses revealed a significant phase transformation from \(\text{MoSe}_2\) to \(K_0\text{Se}\) (e.g., \(K_0\text{Se}_1, K_0\text{Se}_2, K_0\text{Se}_3\)) upon discharging, which could be recovered into pristine \(\text{MoSe}_2\) phase after full charging, and was accompanied by the formation of \(\text{Mo}_{15}\text{Se}_{19}\) and \(\text{Se}\).\(^{329}\)

As mentioned in Section 2.1.3, \(\alpha\text{-V}_2\text{O}_5\) is a typical electrode material for hosting \(\text{Li}^+\) and \(\text{Na}^+\) ions. However, \(K^+\) intercalation and diffusion are difficult reactions primarily owing to the compact interlayer spacing of the \(a\)-\(b\) plane of \(\alpha\text{-V}_2\text{O}_5\) (4.379 Å). To unlock the undesired compact structure for fast \(K^+\) storage, the \(V\)-\(O\) polyhedra in \(\alpha\text{-V}_2\text{O}_5\) crystals were reconstructed using a scalable and facile chemical pre-intercalation method to obtain a single-crystalline bi-layered \(\delta\text{K}_{0.5}\text{V}_2\text{O}_5\) nanobelt with an expanded interlayer space of 9.5 Å (Figure 13c).\(^{1590}\) The resultant \(\delta\text{K}_{0.5}\text{V}_2\text{O}_5\) PIB cathode presented a high reversible capacity of \(\approx 130\) mAh g\(^{-1}\) and an exceptional rate capability of \(\approx 65\) mAh g\(^{-1}\) at a high current density of 10 A g\(^{-1}\) (Figure 13d). Furthermore, the \(\delta\text{K}_{0.5}\text{V}_2\text{O}_5\) cathode which outperformed many state-of-the-art KIB cathodes, presented the highest gravimetric energy densities of \(\approx 400\) and \(\approx 200\) Wh kg\(^{-1}\) at the specific power densities of 0.16 and 30.82 kW kg\(^{-1}\), respectively (Figure 13e).

### 4. Conclusions and Outlook

To summarize, NPM in rechargeable batteries is often achieved via ion substitution, heterogeneous doping, component optimization, and morphology design. Overall, the NPM engineering of redox electrodes is relatively complex, and most electrodes are very sensitive to different external factors, such as the electrolyte system, measurement conditions (e.g., discharge rates and voltage window), surface morphologies, and particles size. Despite the recent significant progress in advanced detection techniques, such as synchrotron irradiation, the direct observation of the multiphase transition processes and effective identification of potential intermediates during cycling are still major challenges. Hence, the specific polymorphism-related storage mechanisms of many reported electrode materials, including the commercially available \(\text{LiFePO}_4\) cathode for LIBs should be further investigated and more studies to elucidate the phase evolution process during discharging–charging are imperative.

#### 4.1. Exploring the Controllable Reversible Polymorphism Transition in Metal-Ion Batteries

The polymorphism transition process of some common metal-ion battery cathode and anode materials has been widely investigated, and some results obtained using different detection techniques are inconsistent or even contradictory, as summarized in Table 1. For LIB cathodes, increasing the \(Li\) content to produce \(Li\)-rich phases and/or introducing heterogeneous atoms to form multicomponent electrode materials are believed to promote the reversibility of the polymorphism transition processes. For SIB cathodes, strategies, such as chemical substitution and sodiation degree control, are similar to those used for LIB cathodes. For PIB cathodes, the reversible \(P2–O2\) and \(P3–O3\) polymorphic transition processes of \(K\)-containing \(P2\)- and \(P3\)-type transition metal oxides, respectively, have been widely studied. \(Mn\)- and \(V\)-based oxides are favored as ZIB cathodes owing to their open frameworks and tunable interlayer spacings. However, most reported ZIB cathodes still present drawbacks. For example, Prussian blue analogues possess stable structures but present low capacities. Moreover, owing to the formation of \(Zn\) dendrites and irreversible discharged species, ZIBs often present poor rate capability and cycling life compared to other types of batteries. Different types of electrode materials, including metal-containing oxides, sulfides, and selenides, and metal-free carbonaceous graphene, have been explored as AIB cathodes. However, the reaction kinetics of most AIBs are relatively sluggish. As summarized in Table 2, for LIB, SIB, and PIB anodes, repeated polymorphism transition steps often result in significant structural changes, which deteriorate cycling stability, particularly for \(Na^+\) and \(K^+\) ions, which present large ionic radii.

In addition to experimental explorations, different theoretical models based on computer calculations and simulations have been proposed to offer clues on the polymorphism evolution process throughout the reactions. However a significant gap still exists between these models and the experimental results. The identification of the safest and most affordable electrode materials with satisfying capacities and controllable reversible polymorphism transition processes is crucial for promoting the rate capability and cycling stability of batteries.
Li–CO2 batteries. The primary drawbacks for achieving attractive battery properties consist of the activation of chemically stabilized CO2, manipulation of the discharge products distribution, and promotion of the reversibility. For example, the presence of the insoluble and nonconductive Li2CO3 discharge product often resulted in the undesired passivation of the cathode and a large overpotential, which greatly lowered the capacity and cycling stability of the batteries. Therefore, the uniform nucleation and growth of the discharge products is crucial for long-life batteries.

Table 2. Summary of nano polymorphism strategies for improving the electrochemical performance of anodes.

| Cathode material | Material synthesis method | Phase transition | Electrochemical performance(a) |
|------------------|--------------------------|-----------------|-------------------------------|
| Amorphous Si/C Nanofiber[260] | Chemical vapor deposition | Amorphous Li5Si to crystalline Li15Si4 | RC = 1500 mAh g⁻¹ (1 A g⁻¹), CRR = 66.7% (100) |
| Nanosized magnetite[254] | Decomposition of Fe(acac)3 with OAc | Spinel Fe3O4 to rocksalt LiFe3O4 | RC = 914 mAh g⁻¹ (926 mA g⁻¹) |
| Spinel Li4Ti5O12[255] | Spray drying | Spinel Li4Ti5O12 to Li2Ti3O7 and Na2Li2Ti12 | RC = 170 mAh g⁻¹ (C/10); CRR = 91.2% (50); CE > 99% (50) |
| MoS2 nanosheets[262] | Peeling off from the single-crystal MoS2 | 2H-MoS2 to Ti-TiMo-S2 | — |
| α-MnS/N,S co-doped nanotube-like carbon[267] | PDA coating followed by carbonization and sulfurization | α-MnS to βMnS | RC = 1415 mAh g⁻¹ (50 mA g⁻¹), CRR = 100% (5000) |
| Microsized MoS2[258] | Ball milling | 2H-MoS2 to Ti-TiMo-S2 | RC = 400 mAh g⁻¹ (50 mA g⁻¹) |
| Spherical MoSe2/N-doped carbon composite[269] | Solvothermal reaction and annealing | MoSe2 to Mo15Se19 | RC = 258.02 mAh g⁻¹ (100 mA g⁻¹), CE = 100% (300) |
| Bilayered δ-K2xV3O9 nanobelts[130] | Chemical preintercalation | δ-K2xV3O9 to n-K3xV3O9 | RC = 131 mAh g⁻¹ (100 mA g⁻¹), CRR = 61.3% (100) |

(a) RC: reversible/maximum/optimized specific capacity (current density); CRR: capacity retention ratio after cycling (cycle number); CE: coulombic efficiency (cycle number).

4.2. Identifying the Desired Polymorphism for Air Electrochemistry in Metal–Air Batteries

NPM studies on metal–air batteries focused on both the electrode materials and discharge products. To date, owing to the complex composition of air and inconsistent electrochemical activities, O₂, CO₂, and N₂ have been analyzed as the active species for metal–O₂, metal–N₂, and metal–CO₂ batteries, respectively. The most widely studied metal–air batteries are Li–O₂ batteries, in which a polymorphism transition between gaseous O₂ and condensed O²⁻ occurs and the discharge products (e.g., Li₂O, Li₂O₂, LiOH, and Li₂CO₃) vary with the system or measurement conditions. Similar problems were identified for Na–O₂ batteries, such as the ambiguous formation mechanisms of NaO₂, the primary discharge product. Some researchers concluded that solid electrolytes favored the stabilization of NaO₂ and prevented the complex side reactions with the liquid electrolyte in liquid Na–O₂ batteries. The performance of other high-valence metal–O₂ batteries, such as Mg–O₂, Al–O₂, and Zn–O₂ batteries, which can be easily operated in aqueous electrolytes, largely depends on the OER and ORR activities of the cathode catalysts. In addition, metal–CO₂ batteries are regarded as promising storage systems for CO₂ fixation and utilization. Moreover, the reusing of greenhouse gas CO₂ is expected to simultaneously address the current energy and environmental crises. To date, many types of electrocatalysts with excellent CO₂ electroreduction activities have been proposed for metal–CO₂ batteries, particularly for Li–CO₂ batteries. The primary drawbacks for achieving attractive battery properties consist of the activation of chemically stabilized CO₂, manipulation of the discharge products distribution, and promotion of the reversibility. For example, the presence of the insoluble and nonconductive Li₂CO₃ discharge product often resulted in the undesired passivation of the cathode and a large overpotential, which greatly lowered the capacity and cycling stability of the batteries. Therefore, the uniform nucleation and growth of the discharge products is crucial for long-life batteries.

4.3. Suppressing Polymorphism for S Electrochemistry in Metal–S Batteries

The polymorphism evolution of S species in metal–S batteries has been thoroughly studied. However, the effective suppression of the undesired shuttle effects is still challenging. The dissolved polysulfides in metal–S batteries tend to migrate from the cathode to the anode regions, leading to the rapid capacity decay and low coulombic efficiency of the batteries. To date, a wide range of strategies for the rational modification of electrode materials, binder types, electrolyte systems, and separators have been used to control the deposition states and reduce the loss of S-based active species. For the widely studied Li–S batteries, the rational design of cathode hosts for trapping polysulfide intermediates via physical confinement or chemical binding, such as the use of hierarchical porous frameworks or chemical functionalization of the electrode surfaces, is the most commonly used strategy.

An important aspect concerning the NPM in Li–S batteries is liquid–solid catalytic conversion process between soluble lithium polysulfides and insoluble species (e.g., Li₂S and Li₂S₄), which is the main reason for the undesired shuttling effect in Li–S batteries.[311] An ideal catalyst should present a high active surface area, high adsorptive capability, good conductivity for electron transfer, excellent catalytic activity, and low production cost. To date, many types of materials, including metals (e.g., Pt, Fe, Ni, and Co) oxides (e.g., MnO₂, TiO₂, VO₂, Fe₃O₄, TiO₂, and WO₃−x), sulfides (e.g., Co₅S₈, Mo₅S₈, MoS₂, WSe₂, Sn₂S₃, VS₄, and Co₅S₈), nitrides (e.g., VN, Co₅N, and TiN), phosphides (e.g., MoP and Ni₃P), carbides (e.g., TiC, NbC, and W₅C₃), metal-free compounds (e.g., black P, doped carbon, BN, and C₅N₅), and their derived heterostructured materials (e.g., TiO₂/MXenes) have been studied as effective catalysts for boosting the oxygen vacancy conversion reactions in Li–S batteries.[312−318] Furthermore, some emerging research directions on this topic include i) the rational design of heterostructured materials (e.g., TiO₂/Ni₃S₄) as bidirectional catalysts for both oxidation and reduction reactions,[134] ii) the use of single atom/clusters-based catalysts (e.g., Zn/MXenes and Mo/CNTs) capable of maximizing catalytic
Despite the significant progress in the field of Li–S batteries, containing hybrid electrolytes, the reversible transport of Li ions, or compounds, multielement, or multicomponent battery performance. However, the presence of multielement or multicomponent species further contributes to the complex polymorphism formation and transition, which are even unstable intermediates and difficult to be directly identified. In this case, theoretical computerized calculations are a powerful tool for predicting the possible polymorphism formation mechanisms and their desired evolution pathways. By combining theoretical calculations with experimental results, more polymorphism-related mechanisms can be easily evidenced, and the preference for phase transition processes can be partly determined.

4.7. Optimizing Polymorphism in Practical Electrolyte and Battery Configurations

Typically, polymorphism is sensitive to the electrolyte system and battery configuration. For example, some undesired surface reconstruction and passivation phenomena always occur in practical batteries and lead to capacity decay and battery failure. By optimizing the electrolyte system, electrode structure, and battery configuration in conformance with the practical requirements, desired surfaces or dual-phase interfaces can be generated to promote desired polymorphism transitions, suppress undesired polymorphism transitions, replace the existing polymorphs with new reversible ones, or even suppress polymorphism. Hence, it is recommended that the polymorphism formation and evolution processes in practical battery models should be carefully confirmed using theoretical calculation, experimental measurements, and visual operando characterization techniques.

4.8. Future Outlooks

NPM offers a good opportunity for understanding the fundamental reaction mechanisms of different rechargeable batteries and could inspire the future material design and battery configurations to meet the increasing demands for day-to-day electronic devices. Although the development of NPM for redox electrodes is still in its infancy, we believe that more details on polymorphism will be revealed as advanced characterization techniques will be developed and the electrochemical properties of electrode materials will be further enhanced using NPM engineering.

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Conflict of Interest

The authors declare no conflict of interest.
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