Modern cities demand a reliable supply of electricity when and where it is needed, therefore a key design for power generators feeding on noncontinuous, nonfuel renewables is installing auxiliary battery-type energy storage systems (BESS). Batteries using Zn ions or Al ions in aqueous electrolytes are highly attractive due to low cost and elemental abundance considerations, but attaining reversibility at a high energy density and long-life operation is challenging. Here, the authors review recent reports of reversible aqueous-electrolyte batteries, focusing on how mechanisms of electrochemical activation, insertion, and conversion occur. Further, key issues related to cation mobility, electrode stability, the formation of electrode–electrolyte interface, and electrolyte decomposition, along with possible solutions or research directions for enabling superior performance of aqueous Zn-ion batteries and Al-ion batteries are explored.

1. Introduction

A global economy growing at an average rate of 3.4% per year, coupled with an ever-increasing population (9 billion by 2040), would ramp up worldwide energy needs by over 30% during the next decade.[1] One proposed solution to this escalating energy demand is a sustainable shift toward nonexhaustive forms of energy like solar, wind, and tidal. However, the intermittent, unpredictable, and dispersed nature of such resources makes them unreliable for on-demand electricity generation and transmission to population/industry centers. Often, electric power can be oversupplied to the grid during off-peak hours and undersupplied during peak hours, as demonstrated by a statistical “duck curve” of the typical energy demand versus the typical energy supply of a solar-powered community throughout the day (Figure 1a).[2]

To remedy this, the integration of battery energy storage systems (BESS) to photovoltaic/turbine modules can enable harvested energy to be released on demand according to consumption patterns.[3-5] When storing energy, BESS can also smoothen weather-dependent fluctuations in generator outputs, facilitating peak shaving and load leveling, on more dynamic timescales.[6,7] Finally, from an infrastructural perspective, modular BESS can achieve grid-level energy storage by connecting many small battery units as in commercial buildings and residential dwellings,[7] or at central power stations with 1–100 MW power capacity.[6,8,9] The megawatt scales involved, however, mean that safety and sustainability evidently form the primary criteria for the mass-produced battery materials, besides low investment cost, long cycle life, and high power/energy density.[10,11]

For large-grid BESS applications, aqueous-electrolyte batteries present practical advantages over conventional nonaqueous batteries: first, manufacturing costs are reduced by elimination of stringent-drying protocols in battery assembly lines. Second, aqueous systems are predicted to facilitate higher power densities owing to the higher ionic conductivity of water-based media,[12,13] while using inexpensive salts. Third, the phasing out of toxic flammable organics by water in battery electrolytes mitigates catastrophic incendiary risks associated with short-circuit failures.[14] Overall essentially, aqueous batteries would offer better cost efficiency, ruggedness, and safety prospects due to the solvation properties, nonflammability, and nonvolatility of water.

However, the gap in demonstrated electrochemical performances between aqueous batteries and nonaqueous batteries is still quite significant. For instance, lead–acid and redox-flow batteries have low energy densities (30 and 25 Wh kg⁻¹), Ni–Cd batteries exhibit persistent memory effects, whereas Ni–Fe electrochemistries tend to produce strong H₂ gassing.[6,8,11,15] In contrast, conventional Li-ion nonaqueous batteries can offer about 260 Wh kg⁻¹ (770 Wh L⁻¹) with stable long-term cycling.[16] Directly translating Li-ion chemistry from a nonaqueous electrolyte to an aqueous electrolyte suggests an attractive BESS candidate system, but the uneven geo-distribution of elemental Li also poses a severe supply risk for disadvantaged countries.[17] Therefore, more abundant and cheaper elements such as Na, K, Mg, Ca, Zn, and Al are preferred for BESS development (Figure 1b), and attracting vast interest for this purpose.

While Na-, K-, Ca-, and Mg-based batteries have been explored,[10,18-23] their volumetric capacities are inferior to those for Zn and Al (Figure 1b),[24] especially when comparing their metallic forms as battery anodes. Zn and Al, being multivalent (MV) ions, can theoretically transfer multiple charges per ion unit. Hence, for this review, we discuss Zn ion- and Al
ion–based chemistries exclusively. Though few reviews document electrode materials and their performances for rechargeable aqueous Zn- and Al-ion batteries,[23,25–27] a comprehensive understanding of ion storage mechanisms remains poorly enunciated. We believe the key to successful implementation of MV-ion batteries requires a simultaneous understanding of various elemental chemistries, in context with each other. Here, we summarize reported electrochemical reactions for Zn-ion and Al-ion electrodes. We compare activation mechanisms for ion transport and the role of water in various crystal lattices, and analyze specific challenges for electrode materials toward enabling aqueous multivalent-ion batteries.

2. Aqueous Rechargeable Electrodes for Zn-Ion Storage

In this review, we discuss rechargeable electrodes which can insert Zn$^{2+}$ ions. Since, electrodes for zinc–nickel batteries,[28,29] alkaline Zn–MnO$_2$ batteries,[30,31] or the hybrid zinc aqueous batteries,[32] store other ions (and not Zn$^{2+}$), we do not discuss these systems here. Broadly, the literature for ZIAB electrodes spans various polymorphs of manganese dioxide,[33–48] vanadium compounds,[49–61] and hexacyanoferrates,[62–65] and we discuss few Zn$^{2+}$ storage mechanisms for these electrodes. Additionally, we also highlight key similarities, missing links in the reaction mechanism, and the role of water, if any.

2.1. Manganese Dioxides

Manganese dioxide is known to exist in many polymorphs. These polymorphs are obtained by arranging MnO$_6$ octahedra in multiple ways. Broadly, the polymorphs can be classified into three types of structures, tunnel-type, layered-type, and spinel-type.

Tunnel-type structures ($\alpha$, $\beta$, and $\gamma$) are formed by corner-sharing MnO$_6$ octahedra. The polymorphs differ in terms of tunnel sizes (Figure 2a–c). $\alpha$-MnO$_2$ shows a tunnel size of 2 $\times$ 2 (wherein 2 $\times$ 2 indicates that each side of the tunnel consists of two MnO$_6$ octahedra); $\beta$-MnO$_2$ has a tunnel size of 1 $\times$ 1 and $\gamma$-MnO$_2$ has both 1 $\times$ 1 and 1 $\times$ 2 tunnels propagating along the same axis. Notably, the tunnels in $\alpha$-MnO$_2$ are larger, and hence cations (e.g., K$^+$ from synthesis precursors) can sit at the tunnel centers and contribute to stabilizing the crystal structure.[66]

On the other hand, layered-type polymorphs consist of sheets of edge-shared octahedra. One example is $\delta$-MnO$_2$ (Figure 2d). Between these sheets, water molecules or other cations can insert, and in the process, further expand the interlayer distance between $\delta$-MnO$_2$ layers. The presence of one layer of water molecules in between two $\delta$-MnO$_2$ layers will result in a birnessite-type structure (Figure 2f), whereas having two layers of water molecules between two $\delta$-MnO$_2$ layers creates a buserite-type structure (Figure 2g).[67]

Besides tunnel-type or layered-type structures, wherein the oxygen sublattice is mostly based on hexagonal-closed packing (HCP), the MnO$_6$ octahedra can form crystal structures wherein the oxygen sublattice is arranged in cubic-closed packing (CCP). The best example is $\lambda$-MnO$_2$ (or more representatively described by unit cells of M$_n$O$_{3n}$). Here, the structure is a spinel-type AB$_2$O$_4$ (where A = vacancy and B = Mn), and neither tunnels nor layers are formed, as shown in Figure 2e.

Pursuing his passion for an electromobile society, he works towards enabling aqueous multivalent-ion batteries.

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2.1.1. Mechanisms of Reversible $\text{Zn}^{2+}$ Storage in $\text{MnO}_2$-Based Cathode Materials

A number of mechanisms governing the electrochemistry between $\text{Zn}^{2+}$ ions and $\text{MnO}_2$ electrodes have been proposed.\textsuperscript{33–48} Although most studies ascribe charge storage to $\text{Zn}^{2+}$ intercalation/extraction mechanisms,\textsuperscript{37,39,43,46–48,68,69} other studies suggest conversion mechanisms based on either reversible proton exchange,\textsuperscript{42} or $\text{Zn}$-mediated $\text{MnO}_2$ dissolution/redeposition.\textsuperscript{70}

We also note that most studies on secondary $\text{Zn}$–$\text{MnO}_2$ batteries preferentially utilize mildly acidic or neutral electrolytes over alkaline electrolytes conventionally used in primary $\text{Zn}$–$\text{MnO}_2$ batteries. Previous attempts in utilizing alkaline electrolytes resulted in poor cycling performances which were attributed to the formation of insulating $\text{ZnO}$ at the zinc anode.\textsuperscript{71,72} The high solubility of zinc in alkaline solutions can cause the zinc metal to dissolve as $[\text{Zn(OH)}_4]^{2-}$ and any nonuniformity in $[\text{Zn(OH)}_4]^{2-}$ concentration at the zinc metal surface can lead to a nonuniform zinc plating during the charging step, resulting in dendrites.\textsuperscript{74,75} Together, the formation of $\text{ZnO}$ phases and zinc dendrites have been suppressed by utilizing mildly acidic electrolytes and a highly reversible electrochemical plating/stripping has been achieved.\textsuperscript{42,76}

$\alpha$-$\text{MnO}_2$: Xu et al. demonstrated a maximum discharge capacity of 210 mAh g\textsuperscript{-1} for an $\alpha$-$\text{MnO}_2$/Zn battery in a mildly acidic $\text{ZnSO}_4$ electrolyte. The battery also exhibited...
an outstanding, consistently near-100% Coulombic efficiency over 100 cycles at a high current rate of 6 C.[45] Analyzing this material, cyclic voltammetry (CV) runs showed well-defined Zn²⁺ insertion and extraction peaks (Figure 3a), whereas ex situ X-ray diffraction (XRD) suggested a tunnel-insertion behavior that converts α-MnO₂ to ZnMn₂O₄ while the electrode is galvanically discharged against Zn metal. This led them to propose the following reaction:

Cathode

\[
\text{Zn}^{2+} + 2e^- + 2\alpha\text{-MnO}_2 \rightarrow \text{ZnMn}_3\text{O}_4
\]  

Anode

\[
\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-
\]

In a separate study, however, Lee et al. deduced a distinct electrochemical insertion mechanism involving H₂O, Zn²⁺, and α-MnO₂.[48] When they indexed transmission electron microscopy (TEM) diffraction patterns from discharged α-MnO₂ cathodes, they surprisingly found ZnMn₁O₃·3H₂O or Zn–birnessite instead of the expected ZnMn₁O₄ (in the birnessite structure, Zn²⁺ is inserted between a water layer and a MnO₆ layer). Curiously, the Mn³⁺ concentrations within the electrolyte also increased with progression of the battery discharge step, and decreased accordingly on a reverse bias. Further, if the discharged battery had this now-Mn-containing electrolyte removed and replaced with a Mn-absent electrolyte, the battery could not be recharged (Figure 3b). Therefore, the electrolyte somehow needed to have Mn³⁺ ions present for battery reversibility to occur, and this supported the idea of Mn³⁺ dissolution/deposition being an integral part of the discharge/charge reactions. Lee et al. proposed that discharging α-MnO₂ caused some Mn⁴⁺ ions forming the tunnel structure to reduce to Mn³⁺. These Mn³⁺ ions formed later disproportionate to Mn⁴⁺ and water-soluble Mn²⁺ which dissolves. It is this partial removal of Mn atoms (via Mn²⁺ dissolution) from the lattice that essentially transforms α-MnO₂ to Zn–birnessite. Notably, the two polymorphs are structurally very similar (Figure 3c), and the α-MnO₂ crystal structure can be regenerated later by adding two edge-shared MnO₆ octahedra for each unit cell between the birnessite layers. However, when Lee et al. followed up on this study, they found that the phase transformation during Zn²⁺ insertion in α-MnO₂ actually involved a Zn–buserite structure (Zn²⁺ inserted between water and MnO₆ layers in a buserite-type structure), instead of a Zn–birnessite structure.[69] The crux is that the two-H₂O-layer Zn–buserite structure becomes unstable when the cathode is dried, and thus transforms to one-H₂O-layer Zn–birnessite by losing its extra water layer, explaining their earlier ex situ findings. On a full cycle, the α-MnO₂ structure was therefore proposed to convert to a Zn–buserite structure and back again to the α-MnO₂ structure.

Beyond intercalation-type mechanisms,[39,43,48,69] Pan et al. proposed a conversion-type mechanism for Zn²⁺ insertion in α-MnO₂.[42] When they indexed transmission electron microscopy (TEM) diffraction patterns from α-MnO₂ cathodes, they surprisingly found ZnMn₁O₃·3H₂O or Zn–birnessite instead of the expected ZnMn₁O₄ (in the birnessite structure, Zn²⁺ is inserted between a water layer and a MnO₆ layer). Curiously, the Mn³⁺ concentrations within the electrolyte also increased with progression of the battery discharge step, and decreased accordingly on a reverse bias. Further, if the discharged battery had this now-Mn-containing electrolyte removed and replaced with a Mn-absent electrolyte, the battery could not be recharged (Figure 3b). Therefore, the electrolyte somehow needed to have Mn³⁺ ions present for battery reversibility to occur, and this supported the idea of Mn³⁺ dissolution/deposition being an integral part of the discharge/charge reactions. Lee et al. proposed that discharging α-MnO₂ caused some Mn⁴⁺ ions forming the tunnel structure to reduce to Mn³⁺. These Mn³⁺ ions formed later disproportionate to Mn⁴⁺ and water-soluble Mn²⁺ which dissolves. It is this partial removal of Mn atoms (via Mn²⁺ dissolution) from the lattice that essentially transforms α-MnO₂ to Zn–birnessite. Notably, the two polymorphs are structurally very similar (Figure 3c), and the α-MnO₂ crystal structure can be regenerated later by adding two edge-shared MnO₆ octahedra for each unit cell between the birnessite layers. However, when Lee et al. followed up on this study, they found that the phase transformation during Zn²⁺ insertion in α-MnO₂ actually involved a Zn–buserite structure (Zn²⁺ inserted between water and MnO₆ layers in a buserite-type structure), instead of a Zn–birnessite structure.[69] The crux is that the two-H₂O-layer Zn–buserite structure becomes unstable when the cathode is dried, and thus transforms to one-H₂O-layer Zn–birnessite by losing its extra water layer, explaining their earlier ex situ findings. On a full cycle, the α-MnO₂ structure was therefore proposed to convert to a Zn–buserite structure and back again to the α-MnO₂ structure.

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were indexable to a MnOOH phase, but not the zinc manganate products described in other reports. Further, elemental mapping using high-angle annular dark-field scanning transmission electron microscopy (STEM-HAADF) indicated that Zn$^{2+}$ ions did not penetrate into the bulk of the nanorods, but instead, were concentrated in flakes surrounding the immediate vicinity of the nanorods (Figure 3e). These flakes were identified as ZnSO$_4$[Zn(OH)$_2$]$_3$ using NMR and XRD. Based on these findings, the authors postulated that during discharge, H$^+$ from the electrolyte converts $\alpha$-MnO$_2$ to MnOOH, whereas OH$^-$ from the electrolyte reacts with ZnSO$_4$ to form ZnSO$_4$[Zn(OH)$_2$]$_3$.

A similar conversion-type mechanism was also proposed by Lee et al.\textsuperscript{[70]} As no shifts in the XRD peak positions were detected between before and after discharge in their $\alpha$-MnO$_2$ nanorod material, the authors speculated that charge storage did not occur via crystallographic Zn$^{2+}$ intercalation. By a combination of XRD analysis, TEM imaging, and the corresponding elemental maps (Figure 4a), the authors further demonstrated that a distinct phase of Zn$_4$(OH)$_6$SO$_4$.5H$_2$O precipitated at the end of electrochemical discharge, which formed mainly only the surface of the $\alpha$-MnO$_2$ nanorods. As this emergent Zn$_4$(OH)$_6$SO$_4$.5H$_2$O phase is widely known to precipitate at high pH values,\textsuperscript{[77]} they tracked pH evolutions in operando, and discovered that the electrolyte pH rose during discharge and dropped during charge, consistent with onsets for Zn$_n$(OH)$_5$SO$_4$.5H$_2$O dissolution/precipitation (Figure 4b). Subsequently, Lee et al. ascribed these pH changes to originate from Mn$^{2+}$ released into the electrolyte as an intrinsic part of the half-cell reaction occurring at the cathode. Essentially, their $\alpha$-MnO$_2$/Zn battery operates on electrolyte equilibrium between two distinct divalent cations. During discharge, Mn$^{2+}$ is released at the cathode, generating a high pH and subsequent Zn$^{2+}$ precipitation out of the electrolyte. During charge, Mn$^{2+}$ from the electrolyte moves back to the cathode, generating a low electrolyte pH and causing Zn$_n$(OH)$_5$SO$_4$.5H$_2$O to dissolve and release the stored Zn$^{2+}$.

$\lambda$-MnO$_2$: $\lambda$-MnO$_2$ has also been considered as a candidate material for ZIAB cathodes as it has been shown to perform reasonably with other divalent cations such as Mg$^{2+}$\textsuperscript{[40,78]} $\lambda$-MnO$_2$ (or spinel Mn$_2$O$_4$) crystals exhibit a cubic phase when all the lattice Mn atoms are in the +4 oxidation state. However, the partial reduction of Mn$^{4+}$ to Mn$^{3+}$ during stepwise discharge results in Jahn–Teller distortions which elongate the MnO$_6$ octahedra along the c-axis, thus triggering a cubic-to-tetragonal conversion in unit cell symmetry.\textsuperscript{[79]}

![Figure 4](https://example.com/figure4.png)

**Figure 4.** A Zn/$\alpha$-MnO$_2$ battery cycled in 1 m ZnSO$_4$. a) TEM image of a discharged $\alpha$-MnO$_2$ electrode, and EDS analyses of detected agglomerates (region I) and nanorods (region II). b) In operando evolution in pH during the first discharge–charge cycle. Reproduced with permission.\textsuperscript{[82]} Copyright 2016, John Wiley and Sons. c) Schematic of the Zn$^{2+}$ migration path in spinel ZnMn$_2$O$_4$ (gray sphere: Zn, red sphere: O, purple octahedra: MnO$_6$). d) The 1st and 2nd charge–discharge cycles for $\beta$-MnO$_2$ at 0.32 C in 3 m Zn(CF$_3$SO$_3$)$_2$. e) XRD data collected at various stages A to J as indicated in (d). Reproduced with permission.\textsuperscript{[39]} Copyright 2017, Springer Nature.
For cubic $\gamma$-$\text{MnO}_2$, Nolis et al. attempted to electrochemically insert $\text{Zn}^{2+}$ into the host lattice but ex situ XRD patterns suggested that the main constituent of the discharged electrode was the parent cubic $\gamma$-$\text{MnO}_2$ phase itself.[88] Additionally, new minor phases including $\text{ZnO}$ and $\text{Zn}_2\text{Mn}_4\text{O}_9$ were also observed. Further using energy dispersive X-ray spectroscopy (TEM-EDS), the authors saw strong elemental segregation in the cathode particles, separately showing Zn-rich phases or Mn-rich phases. These observations, therefore, led them to rule out an intercalation charge-storage mechanism for $\text{Zn}^{2+}$ into cubic $\gamma$-$\text{MnO}_2$.

For tetragonal $\lambda$-$\text{MnO}_2$, the lattice $\text{Zn}^{2+}$ mobility has been probed by simulations. High diffusion barriers for $\text{Zn}^{2+}$ migration have been predicted.[89] Here, it is useful to note that $\text{Zn}^{2+}$ occupies 8a-sites in tetragonal $\text{ZnMn}_2\text{O}_4$ spinel, and in order to move to a neighboring 8a-site, $\text{Zn}^{2+}$ needs to migrate through an intermediate 16c-site (Figure 4c). However, Mn atoms at 16d-sites sit in close proximity to the intermediate 16c-sites, thus exerting electrostatic repulsion and hence disfavoring $\text{Zn}^{2+}$ migration.

To verify this claim experimentally, Knight et al. attempted extracting $\text{Zn}^{2+}$ from tetragonal $\text{ZnMn}_2\text{O}_4$ through chemical methods.[83] They used two different oxidizing agents to chemically extract zinc: 1) NO$_2$BF$_4$ in acetonitrile medium and 2) H$_2$SO$_4$ aqueous solution. One key difference in results between applying these two methods is that unlike the treatment with NO$_2$BF$_4$, the treatment of spinel $\text{ZnMn}_2\text{O}_4$ with H$_2$SO$_4$ aqueous solution can result in dissolution of Mn ions from the spinel $\text{ZnMn}_2\text{O}_4$. This difference leads to a disparity in the amount of $\text{Zn}^{2+}$ ions extracted from the spinel framework. While only a negligible amount of $\text{Zn}^{2+}$ ions could leach out on the treatment of $\text{ZnMn}_2\text{O}_4$ with NO$_2$BF$_4$, an appreciable amount of $\text{Zn}^{2+}$ ions could leach out on treatment of $\text{ZnMn}_2\text{O}_4$ with H$_2$SO$_4$ aqueous solution.

They proposed that, because sulfuric acid treatment partially dissolves Mn atoms from the spinel framework (unlike NO$_2$BF$_4$ treatment), a Mn-deficient spinel structure is obtained. Creation of vacant 16d-sites reduces the electrostatic repulsion between Mn ions and $\text{Zn}^{2+}$ as $\text{Zn}^{2+}$ migrates through the 8a $\rightarrow$ 16c $\rightarrow$ 8a migration path (Figure 4c). Later, Zhang et al. built on this idea of creating Mn vacancies and used spinel $\text{ZnMn}_2\text{O}_4$/$\text{Na}_2\text{O}_3/C$ for ZIB cathodes, which could deliver a high capacity retention of 94% after 500 cycles at a high current rate of 500 mA g$^{-1}$[92].

Other Polymorphs: $\gamma$, $\delta$, $\beta$ polymorphs of $\text{MnO}_2$ have also been studied for ZIB cathode applications.[36,38,43,44] For $\gamma$-$\text{MnO}_2$, the crystal structure exhibits two types of tunnels, 1 × 1 and 1 × 2 (see Section 2.1 and Figure 2c). Using X-ray absorption spectroscopy (XAS), Alfaruqi et al. showed that electrochemical $\text{Zn}^{2+}$ insertion in $\gamma$-$\text{MnO}_2$ induces phase segregation in $\gamma$-$\text{MnO}_2$, with one phase region rich in Mn$^{2+}$ and another phase region rich in Mn$^{3+}$, rather than forming a unitary phase possessing both these Mn oxidation states.[43] In the initial stages of battery discharge ($\text{Zn}^{2+}$ insertion), the HCP-type oxygen sublattice in 1 × 1 tunnels of $\gamma$-$\text{MnO}_2$ shears to a CCP-type sublattice, transforming the material to a spinel $\text{ZnMn}_2\text{O}_4$ (with $\text{Mn}^{3+}$). With further discharge, the 1 × 2 tunnels of $\gamma$-$\text{MnO}_2$ expand slightly and form tunnel-type $\gamma$-$\text{ZnMn}_2\text{O}_4$ (with $\text{Mn}^{3+}$). At the final discharge stages, tunnels of $\gamma$-$\text{Zn}_2\text{Mn}_4\text{O}_9$ formed expand further, transforming it to a layered-type $\text{Zn}_2\text{Mn}_3\text{O}_2$.

For $\delta$-$\text{MnO}_2$, exactly what discharge product forms due to the electrochemical interaction of $\text{Zn}^{2+}$ with $\delta$-$\text{MnO}_2$ remains ambiguous.[38,44] Alfaruqi et al. initially claimed that $\text{Zn}^{2+}$ insertion causes the $\delta$-$\text{MnO}_2$ structure to transform to a mixture of $\text{ZnMn}_2\text{O}_4$ spinel and $\text{Zn}$-$\text{birnessite}$,[39] but they later amended the exact reaction mechanism to be: $\delta$-$\text{MnO}_2$ $\rightarrow$ $\text{Zn}$-$\text{Mn}_2\text{O}_4$ $\rightarrow$ $\text{Zn}$-$\text{birnessite}$ $\rightarrow$ $\text{ZnMn}_2\text{O}_4$ spinel, based on in situ XRD, ex situ XRD, and XAS data.[44]

For $\beta$-$\text{MnO}_2$, Islam et al. showed that $\text{Zn}^{2+}$ insertion results in the formation of many phases: $\text{Zn}$-$\text{birnessite}$, $\text{Zn}$-$\text{Mn}_2\text{O}_4$, and spinel $\text{ZnMn}_2\text{O}_4$ in the bulk material, and $\text{ZnSO}_4.3\text{Zn(OH)}_2.5\text{H}_2\text{O}$ precipitation on the electrode surface.[36] However, XRD results showed that over prolonged charge–discharge cycles, spinel $\text{ZnMn}_2\text{O}_4$ was the predominant bulk phase.

On the other hand, Zhang et al. proposed an alternate $\text{Zn}^{2+}$ insertion mechanism in $\beta$-$\text{MnO}_2$.[39] Through XRD analysis, they pointed out that $\beta$-$\text{MnO}_2$ transformed to $\text{Zn}$-$\text{birnessite}$ at the end of the first discharge step (Figure 4d,e), and ascribed it to $\text{Zn}^{2+}$ and water coinercalation along with manganese dissolution. Thereafter, the subsequent charge–discharge cycling steps showed a reversible intercalation/deintercalation of $\text{Zn}^{2+}$ in the water-containing birnessite framework with a high capacity of $\approx$150 mAh g$^{-1}$ and reversible up to 2000 cycles.

2.1.2. Factors Contributing to Capacity Fading in $\text{MnO}_2$ Polymorphs

The charge–discharge cycling stability for most of the reports on $\text{MnO}_2$ polymorphs is limited to 500 cycles or less (Table 1). Two factors are critical which can lead to degradation in charge–discharge cycling performance of $\text{MnO}_2$ electrodes: 1) irreversible phase transformation to spinel $\text{ZnMn}_2\text{O}_4$ phase, and 2) loss of redox-active Mn ions from the electrode.

Prolonged cycling of $\text{MnO}_2$ polymorphs including $\beta$, $\gamma$, and $\delta$ polymorphs has been shown to generally result in irreversible phase transformations, leading to the emergence of spinel $\text{ZnMn}_2\text{O}_4$ as the dominant phase.[36,38,43,44] The spinel $\text{ZnMn}_2\text{O}_4$ has a very high negative formation energy (≈1293.3 kJ mol$^{-1}$), making the compound very stable and $\text{Zn}$ extraction during the charging step highly unfavorable. The spinel $\text{ZnMn}_2\text{O}_4$ also has very high migration barriers which make lattice mobility of $\text{Zn}^{2+}$ ions very poor.[80,81] Both the factors are believed to account for the observed capacity fading. However, as discussed in the previous subsection on $\lambda$-$\text{MnO}_2$, partial vacancies on the Mn sublattice can reduce $\text{Zn}^{2+}$–$\text{Mn}^{3+}$ electrostatic repulsion during $\text{Zn}$-ion lattice migration and help improve the reversibility of the spinel-$\text{ZnMn}_2\text{O}_4$ crystal structure.[82] Additionally, the $\text{Zn}^{2+}$ diffusion coefficient in Mn-deficient spinel ($0.4 \times 10^{-11}$ cm$^2$ s$^{-1}$, using galvanostatic intermittent titration technique) was found to comparable to the Li$^+$ diffusion coefficient in spinel framework ($\approx 10^{-10}$ cm$^2$ s$^{-1}$).[84] Another reason attributed to the capacity fading is the loss of redox-active Mn atoms from $\text{MnO}_2$ electrodes via $\text{Mn}^{2+}$ dissolution,[44,65,85,86] as discussed in Section 4.1.2. Pan et al. demonstrated that adding $\text{Mn}^{3+}$ in the electrolyte can alleviate this issue.[85] The extra dissolved $\text{Mn}^{2+}$ in the electrolyte shifts the $\text{MnO}_2$/$\text{Mn}^{2+}$($\text{aq}$) equilibrium, suppressing the dissolution of Mn atoms from the electrode into the electrolyte, and hence mitigating the capacity fading issue (Figure 5a). Zhang et al. added a further explanation on the role of preadded $\text{Mn}^{2+}$ in the electrolyte in mitigating the capacity fade.[39] Using the Nernst equation, the thermodynamic potentials for precipitating $\text{MnO}_2$ ($\text{Mn}^{4+}$) and $\text{Mn}_3\text{O}_4$ ($\text{Mn}^{3+}$) from
0.1 M Mn(CF$_3$SO$_3$)$_2$ in 3 M Zn(CF$_3$SO$_3$)$_2$ were calculated to be 1.60 and 1.64 V (vs Zn$^{2+}$/Zn), respectively. Consistent with their calculations, Mn$^{2+}$ from the electrolyte deposited as porous and poorly crystalline integrated MnO$_2$ nanosheets on cathode surface (Figure 5b), when the cathodes were charged above the mentioned voltages. These nanosheets kept the electrode intact, prevented electrode rupture, and hence mitigated the capacity fading, unlike the case where Mn$^{2+}$ was not preaddled in the electrolyte (Figure 5c).

### 2.1.3. Summary

To summarize, MnO$_2$ polymorphs especially the $\alpha$ and $\beta$ polymorphs have shown high capacities with good capacity retentions (Table 1), making them good candidates for BESS. However, the Zn$^{2+}$ storage mechanism for MnO$_2$ polymorphs is still ambiguous. K$^+$, Na$^+$, Mg$^{2+}$, and H$_2$O from synthesis precursors can intercalate into the MnO$_2$ crystals tunnel/layers and change the valence state of Mn in MnO$_2$, making a one-to-one comparison between each study harder.$^{[57,58]}$

Nevertheless, we notice a common trend of phase transformation for most polymorphs to layered buserite or birnessite phases.$^{[36,38,39,41,43,44,48,68,69,89,90]}$ suggesting that layered phases with high interlayer spacing are suitable for Zn$^{2+}$ insertion. We speculate three important steps are responsible for this phase transformation: 1) ingress of water molecules, 2) vacancy creation via Mn$^{2+}$ dissolution, and 3) Zn$^{2+}$ insertion. Phase transformation to structures with high interlayer spacing (7 Å for birnessite$^{[91]}$ and 11 Å for buserite$^{[92,93]}$) also indicate that Zn$^{2+}$ might be entering the crystal with attached water molecules.$^{[69]}$ Therefore, the role of water for Zn$^{2+}$ insertion in the MnO$_2$ polymorphs should be explored.

### 2.2. Vanadium Compounds

Vanadium-based compounds can exist in a variety of crystal structures. This is due to the multiple oxidation states and multiple anion-coordination polyhedra possible for vanadium.$^{[94]}$ One of the polymorphs, zero-V$_2$O$_5$, has been of immense interest for ZIABs, considering its good performance with other multivalent ions such as Mg$^{2+}$ in the water-based electrolyte.$^{[95,96]}$ Additionally, metal vanadates and vanadium-based NASICON (which are isostructural with sodium (NA) Super Ionic CONductor) have also been investigated for ZIABs.$^{[23,26]}$

### 2.2.1. Bilayered Vanadium Pentoxide

Xero-V$_2$O$_5$ exhibits distorted VO$_6$ polyhedra and forms a bilayered structure.$^{[94]}$ These bilayers expand when water molecules insert between them (Figure 6a) to form V$_2$O$_5$·nH$_2$O.$^{[97]}$ The
H₂O interlayer between the V₂O₅ bilayers apparently plays a crucial role in facilitating cation insertion into the zero-V₂O₅ host lattice and enhancing electrode cyclability, in particular via an electrostatic shielding mechanism. The interlayer H₂O reduces the Coulombic interactions between the intercalating cations and the host structure, improving multivalent cation mobilities within crystalline materials during cation insertion.[95,98]

For instance, Yan et al. studied a Zn–V₂O₅/reduced graphene oxide (V₂O₅·nH₂O/RGO) system. They noticed deteriorated cycling performance when the crystal water in the V₂O₅·nH₂O/RGO cathode was eliminated by heating (Figure 6b). This observation indicated that water plays a crucial role in Zn²⁺ insertion, similar to an observation made in the case of Mg²⁺.[99]

An analogous material, Zn₀.₂₅V₂O₅·nH₂O was studied as a cathode in a ZIAB by Kundu et al.[51] The crystal structure of Zn₀.₂₅V₂O₅·nH₂O is very similar to V₂O₅·nH₂O, with one key difference being that the material has also ZnO₆ octahedra along with H₂O molecules in between the V₂O₅ bilayers. Electrochemical Zn²⁺ insertion/deinsertion in 1 m ZnSO₄ electrolyte was demonstrated to be reversible up to 1000 cycles at a high cycling rate of 15 C. The good performance of the battery was attributed to the presence of lattice water. The lattice water could shield the hard divalent-cation charge and lower the activation energy for Zn²⁺ insertion at the interface.[100–102]

Nonetheless, from a crystallographic perspective, there are conflicting reports on the physical effect of water on the V₂O₅
bilayers. While some reports indicate that cation insertion decreases the layer-to-layer distance,[50,52,54,55,102] other reports claim the opposite.[49,53,57,59]

Kundu et al. and numerous other groups,[50,52,54,55,102] observed a lattice contraction along the axis orthogonal to the V2O5 bilayers during Zn2+ insertion, and inferred that Zn2+ insertion causes lattice H2O molecules to be expelled out of V2O5 bilayers (Figure 6c), bringing the V2O5 bilayers closer due to increased electrostatic attractions.

However, other studies demonstrated a lattice expansion instead along the axis orthogonal to the V2O5 bilayers.[49,53,57,59] The interlayer expansion can be caused if the size of intercalating specie is relatively large, which can be attributed to intercalation of Zn2+ along with few water molecules from the electrolyte solvent. Similar observations have also been made during Mg2+ insertion in layered-type materials.[90,103]

2.2.2. Metal Vanadates

Vanadium can coordinate with oxygen atoms in many possible arrangements of tetrahedra or octahedra. For instance, sublattice frameworks composed of VO43− (orthovanadates), V2O74− (pyrovanadates), or [V3O8]nn− polymorphs are possible.[104] The frameworks are charge-balanced with cations of appropriate numbers, sizes, and charges (along with water molecules in some cases), resulting in a metal-vanadate family with general formula MxVyOz (M = metal cation) crystallizing in either a layered- or a tunnel-type structure. In the case of a layered framework, for instance, in LiV3O8, the layers consist of negatively charged [V3O8]− units. Here, nonvanadium metal cations can play an important role in opening and stabilizing the crystal structures. Specifically, the negatively charged layers are held together via the interlayer Li+ ions acting as “pillars”.

For use as ZIAB cathode material, various metal vanadates such as LiV3O8, H2V3O8, Na0.33V2O5, α-Zn2V2O7, Fe5V15O39(OH)9.9H2O, Na2V6O16.3H2O, Ca0.25V2O5·nH2O have been investigated so far.[49,50,52–55,58] However, the Zn2+ insertion mechanism is not unique and may differ for each material. We discuss two examples here in this section: LiV3O8 and Na0.33V2O5.

LiV3O8 (LVO) is comprised of layers of VO5 trigonal pyramids and VO6 octahedra, and lithium as the interlayer bridging atoms.[105] Alfaruqui et al. studied the Zn2+-insertion mechanism in LVO in detail using synchrotron XRD.[50] The initial Zn2+ insertion stage proceeds via a solid–solution route in the LVO phase, as reflected by small shifts in XRD peak positions. The intermediate stage involves a two-phase reaction involving this solid–solution and a stoichiometric ZnLiV3O8 that segregates out. The final stage involves Zn2+ insertion via solid–solution behavior in a Zn0.6LiV3O8 phase (x > 1).

On the other hand, Na0.33V2O5 (NVO) shows a slightly different insertion mechanism, as proposed by He et al. from ex situ XRD data.[58] NVO is also a layered structure but with Na atoms stabilizing the 2D vanadium oxide layers.[106] Unlike the case for LVO, no solid–solution behavior during Zn2+ insertion was observed. Instead, a new phase Zn1−xNa0.33V2O5 (0 < x < 0.96) emerged alongside the pristine Na0.33V2O5 as the discharging proceeded.

2.2.3. Vanadium-Based Polyanionic Structures

The vanadium-based NASICON framework (Figure 7a) consists of VO6 octahedra and PO4 tetrahedra having a general formula of A2V2(PO4)3 where A can be a monovalent/divalent cation. Owing to an inductive effect exerted by phosphate

Figure 7. a) Crystal structure of hexagonal NASICON NaV2(PO4)3 (orange polyhedra: VO6, magenta polyhedra: PO4, green spheres: Na+). b) Crystal structure of nickel hexacyanoferrate, wherein the A-site can be occupied by water molecules or cations. Reproduced with permission.[115] Copyright 2013, ACS. SEM images of different morphologies of zinc hexacyanoferrate c) octahedron, d) truncated octahedron, and e) cubo-octahedron. f) Galvanostatic charge/discharge cycling performance for zinc hexacyanoferrates with particles of different morphologies at 300 mA g−1. Reproduced with permission.[64]  Copyright 2015, Springer Nature.
groups,[107] cations such as Mg$^{2+}$ have been observed to intercalate at a higher potential than vanadium compounds without polyanions.[96,108,109] A similar increase in intercalation potential was also observed when Na$_2$V$_3$(PO$_4$)$_2$ was used as a ZIAB cathode.[64] While the previously discussed xero-V$_2$O$_5$ and metal vanadates exhibited an average intercalation voltage of $\approx$0.7 V (vs Zn$^{2+}$/Zn), Zn$^{2+}$ inserted at a voltage of $\approx$1.1 V (vs Zn$^{2+}$/Zn) in Na$_2$V$_3$(PO$_4$)$_2$.

A fluorophosphate structure such as Na$_3$V$_2$(PO$_4$)$_2$F$_3$ can push the intercalation voltage even higher when compared to Na$_2$V$_3$(PO$_4$)$_2$ due to the presence of the fluorine atom.[110] As a ZIAB cathode, this material has shown an intercalation potential of 1.62 V (vs Zn$^{2+}$/Zn), the highest among any vanadium-based compounds in the literature so far.[60] Moreover, this material has been demonstrated to be highly stable, as evidenced by outstanding capacity retention over 4000 cycles (Table 2).

However, the capacity values for the vanadium-based polyanionic structures are poorer compared to other vanadium-based compounds (Table 2). The reason might be ascribed to high diffusion barriers for Zn$^{2+}$ migration in the host material, similar to theoretical and experimental observations for Mg$^{2+}$ in similar polyanionic structures.[27,111]

### 2.2.4. Summary

When comparing the electrochemical performance of vanadium compounds and MnO$_2$ polymorphs (Tables 1 and 2), we find that even though the intercalation voltages are lower for vanadium compounds, capacities and capacity retentions are better in general, making the energy densities comparable for vanadium compounds and MnO$_2$ polymorphs (Tables 1 and 2), but as Zn$^{2+}$ inserts at a higher potential than vanadium compounds without polyanions, capacities and capacity retentions are better in general, making the energy densities comparable for vanadium compounds and MnO$_2$ polymorphs (Tables 1 and 2), and this material has shown an intercalation potential of 1.62 V (vs Zn$^{2+}$/Zn), the highest among any vanadium-based compounds in the literature so far.[60] Moreover, this material has been demonstrated to be highly stable, as evidenced by outstanding capacity retention over 4000 cycles (Table 2).

### On the other hand, various concerns in this family of materials are yet to be addressed. First, high pseudocapacitive contributions for vanadium compounds between $\approx$48% and $\approx$80% have been registered.[52,56,57,112,113] Even though most studies argue that Zn$^{2+}$ inserts into the bulk based on a shift in XRD peak positions, high pseudocapacitive contributions indicate that most Zn$^{2+}$ ions are stored only at the surface. Second, capacity fading has been observed at low current densities (or prolonged scan duration), which was attributed to vanadium dissolution (see Section 4.1.2).[59] V$^{4+}$ obtained in the cathode during the discharge can oxidize to VO$^{2+}$, a highly water-soluble species, as per the following reaction:[114]

$$
V^{4+} + 2H_2O \rightarrow [VO_2]^+ + 4H^+ + e^-
$$

### 2.3. Prussian Blue Analogs

The Prussian blue material is a metal–organic framework (Figure 7b) with a chemical formula of A$_{MM'}$(CN)$_6$H$_2$O, wherein A is a MV ion or a water molecule, and both M and M’ are transition metals. In previous studies, researchers have demonstrated that the intercalation of various MV ions in these structures occurs at high potentials.[115–117] On similar lines, Zhang et al. showed that rhombohedral Na$_{3}$[Fe(CN)$_{6}$] (or zinc hexacyanoferrate), when used as a ZIAB cathode, can insert Zn$^{2+}$ at a high intercalation voltage of 1.7 V versus Zn$^{2+}$/Zn with a capacity of 52.5 mAh g$^{-1}$.[63]

In these materials, the crystallographic orientation of the electrode active materials is an important parameter for Zn$^{2+}$ insertion. Zn$^{2+}$ insertion into the cathode becomes easier through nanosizing, as the diffusion lengths for cation insertion are markedly reduced, especially with the help of texturing toward the preferred axes for crystallographic intercalation.[36,57] Zhang et al. synthesized Na$_{3}$[Fe(CN)$_{6}$] with different crystallographic facets (Figure 7c–e) and observed a different electrochemical cycling behavior for each morphology.[64]

### Table 2. Electrochemical properties for various vanadium-containing ZIAB cathodes against zinc metal anode.

| Cathode                  | Electrolyte                  | Current collector | Proof of Zn$^{2+}$ insertion | Current rate | Average voltage versus Zn$^{2+}$/Zn | Capacity (% at cycles) | Retention (%) | Ref.   |
|--------------------------|------------------------------|-------------------|------------------------------|--------------|-------------------------------------|------------------------|--------------|--------|
| V$_2$O$_5$·nH$_2$O/RGO (n > 1) | 3 m Zn(CF$_3$SO$_3$)$_2$     | Titanium          | NMR, ex situ XRD             | 6 A g$^{-1}$ | $\approx$0.5                         | $\approx$230           | 91.3% at 900  | [59]   |
| Zn$_{12}$V$_3$(PO$_4$)$_2$·nH$_2$O | 1 m ZnSO$_4$                | XPS, in situ XRD  | 15 C                         | 0.7          | $\approx$230                        | $\approx$91.3% at 1000 | 1000         | [51]   |
| Anhydrous V$_2$O$_5$     | 3 m Zn(CF$_3$SO$_3$)$_2$     | Titanium          | TEM-EDS, XPS, ex situ XRD    | 5 A g$^{-1}$ | $\approx$0.6                        | 91% at 4000            | [57]         |        |
| H$_2$V$_2$O$_5$          | 3 m Zn(CF$_3$SO$_3$)$_2$     | Titanium          | Ex situ XRD, TEM-EDS         | 5 A g$^{-1}$ | $\approx$0.6                        | 80% at 1000            | [53]         |        |
| Na$_{2}$(OH)$_2$VO$_3$   | 3 m Zn(CF$_3$SO$_3$)$_2$     | Titanium          | Ex situ XRD, HRTEM           | 1 A g$^{-1}$ | $\approx$0.6                        | 72% at 1000            | [58]         |        |
| Na$_2$VO$_4$·3H$_2$O     | 1 m ZnSO$_4$                | Stainless steel   | XPS, in situ XRD             | 40 C         | $\approx$0.7                        | 80% at 1000            | [54]         |        |
| α-Zn$_2$V$_3$O$_7$       | 1 m ZnSO$_4$                | Stainless steel   | Ex situ XRD                  | 4 A g$^{-1}$ | $\approx$0.7                        | 85% at 1000            | [49]         |        |
| Fe$_2$V$_2$O$_7$(OH)$_2$·9H$_2$O | 0.3 m Zn(TFSI)$_2$          | Titanium          | In situ XRD, XPS             | 5 A g$^{-1}$ | $\approx$0.6                        | 80% at 300             | [55]         |        |
| Ca$_{22}$V$_2$O$_9$·nH$_2$O | 1 m ZnSO$_4$                | XPS, ex situ XRD  | 80 C                         | $\approx$0.7 | 96% at 3000                        | [52]                   |              |        |
| VO$_3$                   | 3 m Zn(CF$_3$SO$_3$)$_2$     | Titanium          | In situ XRD, HRTEM, XPS      | 300 C        | $\approx$0.6                       | 171 –                  | [112]        |        |
| VO$_3$                   | 3 m Zn(CF$_3$SO$_3$)$_2$     | Carbon paper      | Raman, XPS, ex situ XRD      | 10 mA g$^{-1}$| $\approx$0.7                        | 79% at 10 000          | [113]        |        |
| Na$_2$V$_3$(PO$_4$)$_3$   | 0.5 m Zn(CH$_3$COO)$_2$      | Nickel foam       | Ex situ XRD, HAADF-STEM      | 50 mA g$^{-1}$| 1.1                              | 97% at 100             | [61]         |        |
| Na$_2$V$_3$(PO$_4$)$_3$F$_3$ | 2 m Zn(CF$_3$SO$_3$)$_2$     | Titanium          | XPS, ex situ XRD             | 1 A g$^{-1}$ | 1.62                              | 94% at 4000            | [60]         |        |

$a$No current collector was used, instead a self-standing electrode with carboxymethyl cellulose and styrene–butadiene rubber was used.
in Figure 7f, the charge–discharge cycling performance for different morphologies varied in the following order: cubo-octahedron > truncated octahedron > octahedron. The authors suggested that in a cubo-octahedron, the exposed {100} planes are aligned along the Zn\(^{2+}\)-ion diffusion channels, thus making Zn insertion/deinsertion easier. On the other hand, the octahedron morphology has only {111} planes exposed. The authors argued that along these set of planes, the atomic packing is less dense which exposes more electrode surface to the electrolyte, and thus gives rise to enhanced dissolution of the active material.

However, the capacities of Prussian blue analog materials are poor (≈60 mAh g\(^{-1}\), Table 3) and far lower than Mn-based and V-based cathodes for ZIAB, precluding this material family as a suitable choice for BESS.

### 2.4. Others

Table 4 summarizes the electrochemical performances of some other reported ZIAB electrode materials. A Mo\(_{2.48}\)VO\(_{9.93}\) compound built from MO\(_6\) octahedra (M = V, Mo) which produce tunnels of different sizes (Figure 8a) has been shown to intercalate up to three Zn\(^{2+}\) ions per formula unit.\(^{[118]}\) However, this material has shown a propensity for capacity fading at high cycling rates due to Zn-ion trapping within the ion-transport channels.

Besides transition-metal oxides, many transition-metal chalcogenides also show better MV-ion mobility as we discuss in Section 4.1.1. Mo\(_6\)S\(_8\) is one of these compounds which contains multiple cation insertion sites (Figure 8b). Mo\(_6\)S\(_8\) as a ZIAB cathode has demonstrated a good capacity retention of 90% after 350 cycles at a high cycling rate of 600 mA g\(^{-1}\).\(^{[119]}\) However, the observed intercalation voltage had been poor (≈0.34 V vs Zn\(^{2+}\)/Zn), thus lowering the overall cell energy density.

On the other hand, to date, very few organic materials have been investigated as ZIAB electrodes. Calix(4)quinone, a complicated molecule with open bowl structures and eight C=O groups, was the first organic material to be demonstrated as a viable ZIAB cathode.\(^{[120]}\) Quinone-based compounds store charge via an “ion-coordination” mechanism wherein the positively charged cation coordinates to the negatively charged oxygen atoms along with simultaneous electrochemical reduction of carbonyl groups.\(^{[121]}\) Calix(4)quinone has been shown to form ion coordination with up to three Zn\(^{2+}\) ions at redox-active carbonyl groups (Figure 8c). However, the authors mentioned that the electronic conductivity of the quinone materials are low and hence a low current rate and the incorporation of conductive additives with a percentage as high as 35 wt% had been used to demonstrate reasonable electrochemical performance of capacity 335 mAh g\(^{-1}\) with capacity retention of 87% after 1000 cycles.

### 3. Aqueous Rechargeable Electrodes for Al-Ion Storage

The high volumetric capacity of aluminum along with its low cost and high abundance (Figure 1b) makes it appealing for BESS. Ideally, the development of a battery where Al metal is used as an anode and paired with a cathode material that allows sufficient reversible (de)insertion of Al ion would be a great success in

| Cathode | Electrolyte | Current collector | Proof of Zn\(^{2+}\) insertion | Current rate | Average voltage versus Zn\(^{2+}\)/Zn | Capacity (mAh g\(^{-1}\)) | Retention (% at cycles) | Ref. |
|---------|-------------|-------------------|-------------------------------|-------------|------------------------------------|-------------------------|------------------------|-----|
| Zn\([\text{II}]\text{Fe(CN)}_6\text{Cl}]\text{I}_2\) | 1 M ZnSO\(_4\) | Stainless steel | – | 300 mA g\(^{-1}\) | 1.7 | 52.5 | ≈81% at 100 | [63] |
| Zn\([\text{II}]\text{Fe(CN)}_6\text{Cl}]\text{I}_2\) | 3 M ZnSO\(_4\) | Stainless steel | Ex situ XRD | 300 mA g\(^{-1}\) | 1.73 | 59.2 | 80% at 200 | [64] |
| CuFeCN\(_4\) | 0.2 M ZnSO\(_4\) | Carbon cloth | – | 60 mA g\(^{-1}\) | 1.73 | 52.5 | 96.3% at 100 | [65] |

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**Table 3.** Electrochemical performance for various hexacyanoferrates for ZIAB cathodes against zinc metal anode.

| Cathode | Electrolyte | Current collector | Proof of Zn\(^{2+}\) insertion | Current rate | Average voltage versus Zn\(^{2+}\)/Zn | Capacity (mAh g\(^{-1}\)) | Retention (% at cycles) | Ref. |
|---------|-------------|-------------------|-------------------------------|-------------|------------------------------------|-------------------------|------------------------|-----|
| VS\(_2\) | 1 M ZnSO\(_4\) | – | Ex situ XRD, Raman, XPS, HRTEM-SAED | 50 mA g\(^{-1}\) | =0.65 | 193 | 98% at 200 | [200] |
| Mo\(_6\)S\(_8\) | 1 M ZnSO\(_4\) | Carbon | Ex situ XRD | 600 mA g\(^{-1}\) | =0.35 | 85 | 90% at 350 | [119] |
| Mo\(_{2.48}\)VO\(_{9.93}\) | 0.5 M Zn\((\text{CH}_3\text{COO})_2\) | Carbon strip | HRTEM, STEM-EDS | 10 mA g\(^{-1}\) | =0.4 | 220 | ≈70% at 30 | [118] |
| V\(_{23}\)Al\(_{52}\)O\(_{123}\)(OH)\(_{27}\) | 1 M ZnSO\(_4\) | Stainless steel | Ex situ XRD, X-ray absorption near edge structure (XANES) | 15 mA g\(^{-1}\) | =0.6 | 105 | ≈60% at 50 | [168] |
| Calix(4)quinone | 3 M Zn\((\text{CF}_3\text{SO}_3)\) \(_2\) | Titanium | In situ Raman, in situ Fourier-transform infrared spectroscopy (FTIR) | 500 mA g\(^{-1}\) | 1 V | 335 | 87% at 1000 | [120] |
| Tetrachloro-1,4-benzoquinone | 1 M Zn\((\text{CF}_3\text{SO}_3)\) \(_2\) | Graphite foil | In situ XRD, SEM-EDX | ≈43 mA g\(^{-1}\) | 1.1 | 200 | ≈65% at 30 | [201] |
| Poly(phenylenediamine) | 3 M Zn\((\text{CF}_3\text{SO}_3)\) \(_2\) | Stainless steel | Ex situ FTIR | 0.2 C | 0.95 V | 203 | 86% at 50 | [202] |
the path to reduce the cost of energy storage devices and enable long-term sustainability. Additionally, the use of water over organics as solvent in the electrolyte can significantly bring down the cost of such a battery. However, the development of AIAB remains in a nascent stage and faces certain issues. 1) Currently, Al metal cannot be used in an aqueous electrolyte as an anode, fundamentally due to its electrochemical plating/stripping voltage occurring too far from the stable potential window of water. 2) The electrolyte (AlCl3) developed for AIAB is highly acidic in nature and enhances dissolution of active material and corrosion of auxiliary battery parts. 3) Practically, there is no material reported so far which has shown sufficiently good cycling stability to be used as a high voltage electrode material for AIAB.

In this section, we summarize various implementations of rechargeable AIABs, as reported in the literature. We discuss battery performances focusing on the electrode materials: proposed mechanisms enabling the electrochemical activity for each active material and characterization techniques used to prove Al-ion insertion. Table 5 tabulates the experimental details and the respective performances of AIABs reported to date.

3.1. Titanium Dioxide (TiO2)

TiO2 exists in eight different types of crystal structures, with rutile, brookite, and anatase as the common polymorphs. [122] The anatase TiO2 crystal structure is composed of stacked TiO6 octahedrons that form tunnels, generating suitably sized pathways for cation intercalation (Figure 9a).

In 2012, Liu et al. demonstrated the very first AIAB with reversible intercalation of Al ions in anatase TiO2 nanotubes, [123] which were prepared by anodizing titanium foil (Figure 9b). Their explanation for the newfound electrochemical activity in nanotube TiO2 as opposed to bulk TiO2 was that by virtue of their form factor, nanotubes created shorter ion diffusion paths and a better electrolyte–electrode contact compared to bulk TiO2 during electrochemical testing timescales. Using X-ray photoelectron spectroscopy (XPS) and NMR, Liu et al. showed an electrochemical reduction of lattice titanium (Ti4+ to Ti3+/Ti2+) and suggested the material to be charge-compensated by lattice insertion of Al ions. Further, CV experiments of TiO2 in chloride salts of Al, Mg, and Li showed significantly higher CV peak intensities for the AlCl3 solution (Figure 9c), supportive indeed of a propensity for Al-ion intercalation within the lattice.

However, Liu et al.’s argument that the smaller radius of Al3+, as compared to Li+ and Mg2+ (53.5 pm for Al3+, 76 and 72 pm for Li+ and Mg2+, respectively), resulted in facile intercalation of Al3+ insertion is counterintuitive when considered against two fundamental factors: 1) the hydrated radii of ions and 2) the higher charge density of multivalent ions. The bigger hydrated radius of Al3+ (4.75 Å for Al3+, 4.30 Å for Zn2+, and 3.82 Å for Li+) would most likely make its insertion into TiO2 more difficult, [124] unless the hydration sheath of solvating water molecules are partially or totally stripped from the intercalating ion during the insertion process. Further, Al3+ has a hard charge density, implying that Al3+ would face more resistance during the insertion process, as compared to any other mono-/bivalent molecule of comparable size. Nonetheless, this problem can be mitigated if shielding can be
provided by hydrating water molecules or pre-existing water molecules in the host crystal structure. Thus, given that smaller ions fit easier into lattice tunnels but a shielding effect is necessary for multivalent-ion mobility within the lattice, a partial hydration seems to be the most likely scenario for facile insertion.

In a low pH system, like the one used in Liu et al.’s study (1 m AlCl₃),[123] thermodynamical H₂ evolution should occur near 0 V (vs standard hydrogen electrode (SHE)).[125] For active materials such as TiO₂, for which ion intercalation occurs at a lower voltage (e.g., −0.8 V vs SHE), an applied potential may preferentially induce H₂ evolution over Al-ion insertion. However, Liu et al. observed that Al³⁺ insertion preceded H₂ evolution and occurred at about −1.2 V versus SHE (Figure 9c). A similar observation was made by He et al.,[126] and both Liu et al. and He

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**Table 5.** Electrochemical performance for various materials as AIAB electrode.

| Working Electrode | Composite used | Electrolyte | Current collector | Proof of Al³⁺ insertion | Current rate [mA cm⁻²] | Average voltage [V] (vs SHE) | Capacity [mAh g⁻¹] | Retention (% at cycles) | Ref. |
|-------------------|---------------|-------------|------------------|-------------------------|-------------------------|----------------------------|----------------|----------------------|------|
| TiO₂ nanotube array | TiO₂ nanotube array – 100 | 1 m AlCl₃ | Epoxy resin–coated Ti foil | XPS, NMR | 4 mA cm⁻² | −0.81 | 75 | >100% at 13 | [123] |
| TiO₂ nanoleaves | TiO₂:polyvinylidene fluoride (PVDF): acetylene black (AB) – 80:10:10 | 1 m Al(NO₃)₃ | Pt | XPS, XRD, NMR | 0.05A g⁻¹ | −0.82 | 278.1 | 91.6% at 300 | [126] |
| TiO₂ nanotubes | TiO₂:PVD:AB – 80:10:10 | 1 m AlCl₃ | Ni | – | 0.15 C | −0.84 | 183 | 96.67% at 25 | [130] |
| TiO₂ nanocomposite | TiO₂:PVD:AB – 80:10:10 | 1 m AlCl₃ | Ni | – | 1 C | −0.85 | 170 | 94.12% at 100 | [131] |
| TiO₂ nanotube array | TiO₂ nanotube array – 100 | Different concentrations of Al₂(SO₄)₃, AlCl₃ with NaCl as additive | Epoxy resin–coated Ti foil | XPS | 4 mA cm⁻² | −0.77 | 74.8 | – | [135] |
| G-TiO₂ | G-TiO₂:PVD – 80:20 | 0.25 m AlCl₃ | Stainless steel | XRD | 6.25 A g⁻¹ | −0.73 | 50 mAh g⁻¹ | 64% at 125 | [132] |
| CuFe–PBA | CuFe–PBA:CNT:PTFE – 80:16:8 | 1 m Al(NO₃)₃ | Ti rods | XRD, TEM-EDS | 1 C | 0.72 | 55 | – | [137] |
| Al₀.₂CuFe–PBA | Al₀.₂CuFe–PBA:CNT:PTFE – 80:16:8 | 1 m Al(NO₃)₃ | AC | – | 5 C | 0.5 | 30 | 83.3% at 1000 | [137] |
| CuHCF | CuHCF:AB:PTFE – 80:15:5 | 0.5 m Al₂(SO₄)₃ | Ti mesh | – | 400 mA g⁻¹ | 0.66, 0.83 | 40 | 54.9% at 1000 | [138] |
| CuHCF | CuHCF:SuperP:PVD – 80:10:10 | Nitric acid + 1 m Al(NO₃)₃ | Carbon cloth | – | 5 C | 0.76 | 49 | – | [116] |
| CuHCF | CuHCF:carbon black (CB):Naion – 80:10:10 | 1 mol dm⁻³ AlCl₃ and 1 mol dm⁻³ KCl | Sigracet PV10 | – | 20 C | 1.5 (full cell) | 10 mAh g⁻¹ | 90% at 1814 | [203] |
| Xero–V₂O₅ | Xero–V₂O₅:polytetrafluoroethylene (PTFE):carbon black | 1 m AlCl₃ | Carbon paper | XPS, XRD | 60 mAh g⁻¹ | 0.48 | 120 | 62.5% at 13 | [139] |
| Exfoliated graphite | Graphite:AB:PTFE – 80:10:10 | Al₂(SO₄)₃/Zn(CHCOO)₂ | Carbon rod | HRTEM, SAED, XRD | 0.5 A g⁻¹ | 0.24 | 80 mAh g⁻¹ | 94% at 200 | [141] |
| Na₃V₂(PO₄)₃ | NVP:CB:PVD – 80:10:10 | 0.1 m AlCl₃ | – | Electron probe micro analysis (EPMA), NMR, XRD, XPS | 60 mAh g⁻¹ | 0.62 | 100 | 40% at 40 | [145] |
| PPy-coated MoO₃ nanotubes | MoO₃:AB:PTFE – 80:10:10 | 0.5 m Al₂(SO₄)₃ | Carbon rod | EDS, XRD, XPS | 2 A g⁻¹ | – | 30 Wh kg⁻¹ | 93% at 1800 | [146] |
| 2D Ti₃C₂Tₓ | Ti₃C₂Tₓ: onion-like carbon (OLC):PTFE – 85:10:5 | 1 m Al(NO₃)₃, Al₂(SO₄)₃ | Freestanding | – | – | – | – | – | [147] |

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In a low pH system, like the one used in Liu et al.’s study (1 m AlCl₃),[123] thermodynamical H₂ evolution should occur near 0 V (vs standard hydrogen electrode (SHE)).[125] For active materials such as TiO₂, for which ion intercalation occurs at a lower voltage (e.g., −0.8 V vs SHE), an applied potential may preferentially induce H₂ evolution over Al-ion insertion. However, Liu et al. observed that Al³⁺ insertion preceded H₂ evolution and occurred at about −1.2 V versus SHE (Figure 9c). A similar observation was made by He et al.,[126] and both Liu et al. and He
et al. attributed this increased electrochemical stability of H_2O to the strong solvation interactions between Al ions and H_2O. Additionally, an increased H_2 overpotential can result from varying bonding strengths of hydrogen species on different electrode surfaces, as observed for various metal surfaces.[127,128] Thus, surface-dependent overpotentials for proton reduction play a significant role in expanding the electrochemical stability window of water, making it possible to use low voltage materials like TiO_2.

By modifying anatase TiO_2 to a mesoporous nanoleaves morphology, He et al. demonstrated an improved discharge capacity of 278 mAh g^{-1} at 0.05 A g^{-1} in 1 M Al(NO_3)_3 aqueous solution.[126] Mesoporous TiO_2 nanoleaves (Figure 9d), prepared by solution plasma processing, had an average particle size of 50 nm in length and 10 nm in width. Each leaf was made up of many small particles arranged in an orderly manner, sharing the same crystallographic orientation. The initial discharge curve for Al-ion insertion in TiO_2 (Figure 9e) showed similar behavior as proposed for Li-ion storage in TiO_2.[129] He et al. observed three different voltage regions (A, B, and C) in the initial discharge curve (Figure 9e). Region A consisted of a monotonic voltage drop which hinted toward the formation of a homogeneous solid solution of Li and TiO_2. Following region A, a plateau (region B) is observed indicative of two-phase bulk intercalation. Following this, two different mechanisms occur in region C. At high current rates, reversible interfacial storage becomes dominant, whereas at low current rates, irreversible bulk intercalation takes place.

Using XPS, He et al. confirmed the concomitant increase in Al^{3+} concentrations with Ti reduction (Ti^{4+} to Ti^{3+}) in the discharged sample. Additionally, in region A and region B of the charge-discharge curve (Figure 9e), a linear shift in the lattice parameter was observed during in situ XRD measurements which indicated insertion of foreign species into the TiO_2 lattice. He et al. claimed that the amount of oxygen vacancies in TiO_2 nanoleaves was more than what was present in commercial TiO_2, and the missing oxygen was probably due to replacement by N and H atoms during plasma processing, although a definitive mechanism had not been provided. It was further speculated that the presence of N and H helped to suppress the irreversible further reduction of Ti^{3+} to Ti^{2+} during Al^{3+} insertion. Of note, the reduced gaps between the peak-onset voltages of the cathodic and anodic sweeps for these TiO_2 nanoleaves (Figure 9f) indicated that Al^{3+} insertion/extraction occurred more readily in anatase TiO_2 nanoleaves as compared to commercial samples. He et al. also showed that substantial proton insertion was unlikely by showing: 1) negligible water loss due to intercalated protons during thermogravimetric analyses of electrodes and 2) no changes in O1s XPS spectra at different stages of cycling (after the 1st discharge step and the subsequent 1st charging step). With a capacity of 278 mAh g^{-1} and stable retention of 91.6% over 300 cycles, this is by far the best electrode performance reported for AIAB. He et al. attributed the improved electrochemical performance of anatase TiO_2 nanoleaves to nanoparticle ordering within the nanoleaves which aided lattice intercalation, increased surface areas at the electrode–electrolyte interfaces, and the structural robustness of TiO_2.

In a similar work to He et al., Kazazi et al. highlighted the importance of short diffusion paths and accessibility of electrons.
and electrolyte ions to the intercalating host material, by synthesizing highly porous and high surface area TiO₂ nanospheres and testing it in 1 m AlCl₃ for Al insertion. This material showed an initial capacity of 183 and 108 mAh g⁻¹ at a low rate of 0.15 C and a high rate of 6 C, respectively. In continuation, Kazazi et al. made an improved material in the form of TiO₂/carbon nanotube (CNT) nanocomposite anode material, which showed an enhanced and more stable capacity (225.5 and 135 mAh g⁻¹ at 0.15 C and 6 C, respectively) as compared to the pristine TiO₂ nanospheres in their previous work. Kazazi et al. attributed this improved performance to the enhanced surface area and conductivity network around TiO₂ due to CNT incorporation.

Exploring the same concept of performance enhancement due to better electrical conductivity, Lahan et al. tested Al insertion in anatase TiO₂ with different conductive additives (graphene, CNT, and Ag). Graphene–TiO₂ composites showed clear anodic and cathodic peaks in 1 m AlCl₃, whereas pure TiO₂ without any conductive additives did not. Increasing electrochemical activity was observed in the following order: graphene–TiO₂ > CNT–TiO₂ > Ag–TiO₂ > TiO₂. Interestingly, Lahan et al. observed the same trend in electrical conductivities. Lahan et al. believed that limitations in electronic conductivity could be manifested by observing the Al³⁺-ion diffusion coefficient and estimated it using Randles–Sevcik equation, again observing the same trend as electrochemical activity/electrical conductivity. Electrochemical impedance spectra (EIS) also showed minimum charge carrier resistance in pristine and cycled samples of TiO₂.

Figure 10. The respective CVs for a) a graphene–TiO₂ composite and b) TiO₂, in 1 m AlCl₃ electrolyte at a scan rate of 5 mV s⁻¹. Reproduced with permission. Copyright 2017, ACS. c) Ex situ XRD patterns of graphene–TiO₂ nanoparticle electrodes after the 1st and 5th negative-wave (from −0.4 to −1.5 V vs Ag/AgCl) and positive-wave CV scans at 5 mV s⁻¹, in 0.5 m AlCl₃ electrolyte (XRD peaks for anatase TiO₂ is denoted as “A”). Reproduced with permission. Copyright 2018, Springer-Verlag GmbH Germany. d) Typical cyclic voltammogram curves of the as-prepared anatase TiO₂ nanotube arrays at 10 mV s⁻¹ in electrolytes of 0.25 M Al₂(SO₄)₃ with varying concentrations of NaCl added. Reproduced with permission. Copyright 2014, Elsevier Ltd. e) Faradic resistance (R_F) of TiO₂ electrodes as a function of polarization time in chloride-based and sulfate-based electrolytes at various pH. Reproduced with permission. Copyright 2016, Elsevier Ltd.
graphene–TiO₂. Lahan et al. argue that the Faradic reaction that TiO₂ undergoes is a coupled reaction of both the charge carriers: Al³⁺ and e⁻. Therefore, an adequate transport of electrons is also needed for facile diffusion of Al³⁺ in TiO₂. The presence of the conductive additive, graphene, aids in ensuring a sufficient supply of electrons. This study highlighted the necessity of sufficiently conducting additives in electrodes for Al-ion intercalation materials. In continuation to this work,[133] Lahan et al. further elucidated a successful reversible Al³⁺ intercalation based on their detection of two Al-based phases (Al₂TiO₅ and Al₂Ti₇O₁₅) in the discharged electrode within the graphene-wrapped TiO₂ nanoparticles, which were not detected in the charged state (Figure 10c).

Besides electronic conductivity, the electrolyte anion may also play an important role in assisting the insertion of Al ions into host materials. Most of the nonaqueous Al-ion batteries investigated so far cycle only in chloride-based electrolytes,[134] whereas none or only weak electrochemical activities have been observed in sulfate- and nitrate-based aqueous electrolytes (Table 5). Experimenting with an array of electrolytes, Lahan et al. observed weaker electrochemical activity for Al³⁺ insertion into TiO₂ in Alₓ(SO₄)₃ electrolytes and no activity in Al(NO₃)₃ electrolytes, as compared to the strong activity in AlCl₃ electrolytes.[132] In an attempt to understand the role of Cl⁻ ions, Liu et al. performed a similar study on TiO₂ nanotube array in electrolytes with varied anionic species.[135] Electrodes based on TiO₂ nanotube arrays were observed to be electrochemically inactive for Al³⁺ insertion in Al₂(SO₄)₃ electrolytes, unlike in AlCl₃ electrolytes where an obvious pair of reversible redox peak was observed. Liu et al. also observed an increase in electrochemical activity with increasing concentrations of NaCl in Al₂(SO₄)₃ (Figure 10d), suggesting indeed some role of Cl⁻ ions in the intercalation process. However, as opposed to expectations, no chloride peaks were observed on the electrode surface by XPS. The mechanism of how Cl⁻ ions assist in the electrochemical insertion of Al ions thus still remains inconclusive and remains an open question.

Though Al-ion insertion into TiO₂ has been shown possible, the intercalation occurs at low voltages relative to the SHE which may make TiO₂ materials particularly vulnerable to proton cointercalation. Sang et al. investigated the influence of H⁺ on the electrochemical behavior of TiO₂ nanotube arrays in a series of aqueous solutions with coexistent H⁺–Al³⁺ ions.[136] Two electrochemical mechanisms for the reaction of H⁺ on/in TiO₂ nanotubes were proposed: 1) proton insertion with parallel hydroxylation–dehydroxylation process occurring on the TiO₂ surface at the initial stages of cycling or 2) H⁺ intercalation–deintercalation into TiO₂ without OH⁻ mediation. It was speculated that the intercalation phenomenon will dominate at higher H⁺ concentrations. Using EIS, Sang et al. studied polarization resistances (Rₛ) as a function of polarization time in chloride- and sulfate-based electrolytes at varying pH values (Figure 10e). Three different observations and corresponding inferences were made from this study: 1) a typical Rₛ versus time curve showed an initial increase and subsequent decrease in Rₛ. This was attributed to the fact that initially, hydroxylation was dominant which suppressed ion intercalation but at a later stage, H⁺/Al³⁺ ion could begin intercalating along with increased conductivity within the active material network; 2) the evolution of Rₛ versus time exhibited a faster response in a chloride-based electrolyte, as compared to a sulfate-based electrolyte at the same pH. This indicated that surface hydroxylation–dehydroxylation and/or intercalation–deintercalation occurred more readily in the presence of Cl⁻, same as previously observed by Liu et al.;[133] 3) for a fixed anion, the Rₛ values were found to be less for electrolyte with lower pH. This indicated that H⁺ was more active as compared to Al³⁺. Therefore, Sang et al. suggested the use of a lower acidity (pH ≥ 3) electrolytes to ensure effective insertion of Al³⁺ in TiO₂ nanotube arrays.[136]

Based on reports so far (Table 5), the nanoleaves morphology for TiO₂ seems the best for the application of TiO₂ as an anode material for AIAB. Though reports have demonstrated positive effects on Al-ion electrochemistry by nanosizing and incorporation of conductive additives, the roles of Cl⁻ and H⁺ ions in the insertion process are not yet clear. More studies focused on electrolyte optimization and the formation of the electrode–electrolyte interface can lead to insights for further enhancing the stability and capacity of this material, taking it one step closer to commercialization at a larger scale.

3.2. Copper Hexacyanoferrate (CuHCF)

CuHCF nanoparticles were reported as the first high voltage (0.72 V vs SHE) active material for AIABs.[137] In their setup, Li et al. first aluminated a fresh CuHCF electrode by discharging it to 0.1 V (vs Ag/AgCl) in 1 M Al(NO₃)₃ and later used it to configure a symmetric cell consisting of aluminated CuHCF as counter electrode against a pristine CuHCF as working electrode, in 1 M Al(NO₃)₃. Upon discharging (samples A–C) and subsequent charging (samples D–F), pristine CuHCF showed increasing and decreasing amounts of Al/Cu ratio, respectively (Figure 11a). Elemental maps of discharged CuHCF, sample C, (Figure 11b) showed the Al ion to be uniformly distributed. The total charge transferred amounted to 6 electrons or 2 Al³⁺ ions per formula unit. This charge number is consistent with findings for Na-, K-, and Mg-ion insertion in CuHCF,[137] and as Li et al. argues, suggests that the charge capacity of CuHCF is limited by the availability of electrons from the Fe²⁺/Fe³⁺ redox pair of the HCF sublattice.

Similar to the case for TiO₂, hydrating water molecules may have played a significant role during the intercalation process into CuHCF. Li et al.,[137] Liu et al.[138] and Wang et al.[136] all observed broadened CV peaks (similar to Figure 11c) for Al-ion insertion in CuHCF, hinting toward a complex insertion mechanism and poor insertion kinetics. Liu et al. hypothesized poor kinetics to be a result of bigger sized solvated Al ion trying to intercalate into the host material framework. At the same time, Liu et al. hinted toward probable desolvation phenomena occurring during insertion. Liu et al. argue that hydrated Al³⁺ radius (~4.8 Å), bigger than the radius of channels (1.6 Å) connecting the site of guest ions in CuHCF, must desolvate in order to intercalate. A similar argument was made by Wang et al., wherein, they attributed broadened CV peaks to either different degrees of dehydration occurring during the insertion process or ions occupying multiple crystallographic sites in CuHCF.
Pre-existing zeolitic water (as discussed in Section 2.3) in CuHCF can also shield the high charge density on Al\(^{3+}\) from the host material and increase Al\(^{3+}\) mobility. Wang et al.’s study on various monovalent, divalent, and trivalent ions for CuHCF in nitrate-based aqueous solutions corroborates the same proposition.\(^\text{116}\) Based on the refinement results and negligible change in insertion chemistry for different cations, Wang et al. suggested a high degree of charge screening either by water molecules in the hydration shell or pre-existing crystal water in host structure.

### 3.3. Vanadium Oxide (Xero-V\(_2\)O\(_5\))

The layered V\(_2\)O\(_5\) structure along with a high V\(^{5+}/\)V\(^{4+}\) redox potential makes it suitable as an AIAB cathode. González et al.
showed reversible intercalation of Al ions into V$_2$O$_5$ xerogels, in 1 m AlCl$_3$ aqueous electrolyte.\cite{139} XPS results confirmed the intercalation of Al ion and concomitant reduction of the average oxidation state of lattice vanadium in discharged V$_2$O$_5$ cathodes. The ex situ XRD results (Figure 11d) of electrodes obtained at different stages of discharging indicated progressive amorphization of V$_2$O$_5$. González et al. also observed a significant drop in gravimetric capacity on cycling V$_2$O$_5$ at 60 mA g$^{-1}$, which worsened at a higher cycling rate of 200 mA g$^{-1}$ (Figure 11e). González et al. believed this deteriorated stability to be a result of structural amorphization caused by cointercalating Al$^{3+}$ and H$_2$O. They proposed a side-reaction mechanism wherein inserting Al ion reduces a proportionate stoichiometry of vanadium to a lower oxidation state, forming a hydrated Al–V complex responsible for the loss of crystallinity.

$$\frac{x}{3} \text{Al}(\text{H}_2\text{O})_{x/3} + (\text{V}^{3+})_2 \text{O}_3 + xe^- \rightarrow (\text{Al}^{3+})_{x/3} [(\text{V}^{3+})_2 (\text{V}^{4+})_{2-x}] \text{O}_3.n\text{H}_2\text{O}$$

(4)

3.4. Graphite

Graphene in its different forms, namely, foam, film, and powder, has shown exceptional power density and cycling stability for nonaqueous Al-ion batteries.\cite{140} It can be engineered by creating defects or introducing functional groups so as to accommodate large-sized intercalating ions. Wang et al. reported an exfoliated graphite material for Al-ion batteries,\cite{141} which is produced by a two-step process: first, H$_2$O and NO$_3^-$ molecules are electrochemically inserted into pristine graphitic layers; second, under subsequent application of appropriate voltages, H$_2$O could be oxidized to O$_2$ while NO$_3^-$ reduced to NO, thus producing sufficient gaseous pressure to exfoliate graphitic layers. These exfoliated sheets could then be processed into a cathode and paired with a Zn foil anode, and successfully cycled in an aqueous Al$_2$(SO$_4$)$_3$/Zn(CH$_3$COO)$_2$ electrolyte. When the electrolyte was modified to eliminate all Al ions in solution, however, Wang et al. did not observe CV peaks (Figure 12a). They thus concluded that the electrochemical activity in Al$_2$(SO$_4$)$_3$/Zn(CH$_3$COO)$_2$ originated from Al-ion intercalation alone and that other spectator ions (Zn$^{2+}$, H$^+$, CH$_3$COO$^-$, or SO$_4^{2-}$) did not cointercalate. With discharge, graphite sheets also exhibited an increase in interlayer distances by 0.5 Å (Figure 12c,e), whereas selected area electron diffraction (SAED) patterns indicated new phases which were not present before discharge (Figure 12d,f). This gave strong evidence of the crystallographic insertion of foreign species into the graphitic layers. However, in the deep interior area of the discharged graphitic nanosheet, the high-resolution transmission electron microscopy (HRTEM) image and SAED pattern (Figure 12g,h) were identical to that of the pristine sample.

Figure 12. a) CV curves of graphite nanosheet in different electrolytes at 1 mV s$^{-1}$. b) Ultrafast charging/discharging in Zn/graphite nanosheet battery in Al$_2$(SO$_4$)$_3$/Zn(CH$_3$COO)$_2$. c) HRTEM image of original graphite nanosheet electrode (interlayer spacing: 0.34 nm) and d) the corresponding SAED image. e) HRTEM image of the discharged graphite nanosheet electrode near surface (interlayer spacing: 0.39 nm) and f) the corresponding SAED image. g) HRTEM image of the discharged graphite nanosheet in the bulk (interlayer spacing: 0.34 nm). h) The corresponding SAED image. Adapted with permission.\cite{141} Copyright 2016, ACS.
essentially indicating the intercalation of hydrated Al ion occurred readily on the surface but not in the interior graphite bulk. Nevertheless, Wang et al. showed an exceptionally fast charging time of 110 s for this material, obtaining a discharge capacity of 60 mAh g\(^{-1}\) at a rate of 2 A g\(^{-1}\) (Figure 12b). To obtain an improved capacity by allowing deep insertion of Al\(^{3+}\), modified forms of graphene may aid as they have in the past for other materials.\(^{[142-144]}\)

### Table 6. Composition and corresponding lattice parameters of NVP (pristine and cycled). The theoretical composition accounts for all the electrons that flowed through the electrochemical cell during cycling. Experimental compositions were obtained by EPMA. Lattice parameters are from refinement of XRD data. Reproduced with permission.\(^{[145]}\) Copyright 2017, Elsevier Ltd.

| NVP electrode          | Theoretical composition | Experimental composition | Lattice cell parameters [Å] |
|------------------------|-------------------------|--------------------------|-----------------------------|
| Raw                    | Na\(_2\)V\(_2\)(PO\(_4\))\(_3\) | Na\(_2.8\)V\(_2\)(PO\(_4\))\(_3\) & n | \(a = 8.735(5)\) |
|                        |                         |                          | \(c = 21.82(1)\) |
| After first charge     | Na\(_1\)V\(_2\)(PO\(_4\))\(_3\) | Al\(_{0.06}\)Na\(_{0.94}\)V\(_2\)(PO\(_4\))\(_2\) & n | \(a = 8.401(1)\) |
|                        |                         |                          | \(c = 21.444(4)\) |
| After charge + discharge | Al\(_{0.3}\)Na\(_{1}\)V\(_2\)(PO\(_4\))\(_3\) | Al\(_{0.25}\)Na\(_{0.81}\)V\(_2\)(PO\(_4\))\(_2\) & n | \(a = 8.51(1)\) |
|                        |                         |                          | \(c = 21.81(3)\) |

3.5. \(\text{Na}_3\text{V}_2\text{(PO}_4\text{)}_3\)

NASICON-type \(\text{Na}_3\text{V}_2\text{(PO}_4\text{)}_3\) (NVP) was studied by Nacimiento et al. with rigorous detail using 0.1 M AlCl\(_3\) aqueous electrolytes.\(^{[145]}\) NVP/carbon nanocomposites were prepared by wet ball-milling in order to 1) enhance the conductivity and 2) slow down dissolution of NVP in the electrolyte. By using multiple characterization techniques, Nacimiento et al. presented a convincing case of Al-ion insertion into NVP. First, semiquantitative microanalysis was used to determine the composition of raw, first charged, and discharged samples, and agreed well with the corresponding theoretical composition calculations obtained from electrochemical data (Table 6). Second, ex situ XRD results showed a contraction/expansion cycle for the crystallographic unit cell, consistent with ion intercalation/deintercalation. Third, XPS results indicated high Al peak intensity in discharged samples, whereas vanadium peaks reversibly shifted to higher and lower energy values following battery charge and discharge, respectively. Fourth, a NMR study directly confirmed the presence of lattice-inserted Al ions, along with surface-accommodated Al ions. Based on all these characterizations, Nacimiento et al. thus proposed a mechanism wherein NVP loses sodium ions during the first charging cycle, while subsequent discharging leads to both bulk intercalation and surface storage of Al ions, both of which contribute to the measured specific capacity. Though the cycling stability of NVP in this study was nothing exceptional, multiple characterization techniques complimenting each other have very clearly demonstrated a successful Al-ion insertion.

3.6. Others

Wang et al. reported Al-ion intercalation/deintercalation for polypyrrole (PPy)-coated MoO\(_3\) nanotubes.\(^{[146]}\) Though ex situ XRD showed a change in the interlayer spacing of MoO\(_3\) layers after discharging (which often suggests the possible intercalation of ions), the electrochemical behavior was later elucidated to be primarily capacitive in nature. Interestingly, the formation energy for MoO\(_3\) with Al inserted is predicted to be comparatively lower than for Na/Li-inserted MoO\(_3\), according to first-principle simulation. The possibility of Al-ion insertion in 2D Ti\(_3\)C\(_2\)T\(_x\) (where T is O, OH, and/or F surface termination group) layers was also explored in 2013, wherein Lukatskaya et al. demonstrated capacitive interactions of Al ions with 2D Ti\(_3\)C\(_2\) layers, albeit without comprehensive evidence of Al-ion insertion.\(^{[147]}\)

### 4. Challenges and Solutions

Grid-scale BESS systems can be cumbersome to install or decommission, hence achieving long-term stability (e.g., end-of-life at \(>10\) 000 cycles) at a high energy density is essential for deployed batteries. At a fundamental level, batteries store energy via the redox coupling of the active materials within the negative electrode and the active materials within the positive electrode. However, for energy conversion to occur, auxiliary battery components such as the electrolyte and the current collector must be in perpetual interaction with the active materials. Consequently, a comprehensive understanding on electrode behavior, electrode–electrolyte interface formation, and current-collector compatibility is mandatory for any battery development. A poor control of deleterious side reactions generated within ZIABs and AIABs would cripple any prospects for their mainstream adoption in electric grids. Here, we present key challenges in detail and propose possible solutions for achieving minimal degradation at the maximum charge capacities/voltage outputs.

#### 4.1. Electrode Material

Novel electrode materials designed for ZIABs and AIABs have shown reversible electrochemistry. However, they remain fraught with major issues such as: 1) the limited mobilities of multivalent cations within host-structure lattices; 2) the limited cycling stability of electrodes; and 3) proton/hydroxide coininsertion. Moreover, at the electrodes, uncontrolled dissolution of redox-active transition-metal components, and \(\text{O}_2\)-driven parasitic reactions (from dissolved \(\text{O}_2\) in the electrolyte) can also have catastrophic consequences on ZIAB and AIAB battery performances.

#### 4.1.1. Limited Cation Mobility in Solid-State Electrodes

The high charge-to-radius ratio of MV cations makes them highly polarizing, which in turn can limit their solid-state diffusivities.\(^{[95]}\) With poorer solid-state kinetics, the transfer of MV
ions from a high-ion-mobility electrolyte (a liquid medium) to a low-ion-mobility electrode (a solid-state medium) can cause current responses to be progressively dominated by pseudocapaci-
tive effects on electrode surfaces rather than by ion intercalation
into bulk crystal structures. Such behaviors have been reported by
multiple studies on ZIABs,[52,56,67,112,113] and AIABs.[116,118] How
strongly the MV-cation mobilities are limited can depend consid-
erably on the crystal structure of the host material.

On a first-principle basis, Rong et al. simulated host mate-
rials which normally support Li-ion intercalation (spinel
Mn$_2$O$_4$, olivine FePO$_4$, layered NiO$_2$, and orthorhombic δ-V$_2$O$_5$)
for MV-ion insertion.[148] They point out that every intercalating
cation has an energetically preferred anion-coordination envi-
ronment based on its size and charge. Because of this, a cation
already occupying such a preferred coordination environment
in a host material will be energetically very stable, requiring
the most energy to be dislodged from its ground-state position
and overcome the higher migration barriers for an effective net
ion jump. For instance, they predicted that the Zn$^{2+}$ mobility in
spinel Mn$_2$O$_4$ (Figure 13a) would be reduced as Zn$^{2+}$ occupies
tetrahedral sites in ZnMn$_2$O$_4$ at room temperature (the tetra-
hedral configuration being the most energetically stable coor-
dination for Zn$^{2+}$ within an oxygen sublattice). This prediction
was later verified experimentally by Knight et al. through actual
electrochemical measurements.[81]

Figure 13. a) Migration energies calculated using first-principles simulations for various cations in spinel Mn$_2$O$_4$. b) Migration path for cation (red sphere) between two tetrahedral sites via octahedral site in spinel Mn$_2$O$_4$. c) Migration energies calculated for various cations in δ-V$_2$O$_5$ structure. Reproduced with permission.[148] Copyright 2015, ACS.

Besides the stable coordination environments of the interca-
lating cation within the lattice, the transitory coordination envi-
ronments involved in the cation migration path can also dictate
the level of cation mobility. Rong et al. compared the migration
energies of mobile cations in layered V$_2$O$_5$ and spinel Mn$_2$O$_4$
crystal structures using first principles. During ion hopping,
the coordination configuration changes between octahedra
and square pyramids in layered V$_2$O$_5$, whereas the coordina-
tion configuration changes in spinel Mn$_2$O$_4$ (Figure 13b) are
between octahedra and tetrahedra.[149] A change from a coor-
dination number of 6 to 5 to 6 leads to lower ion-migration
barriers compared to a change from a coordination number of
6 to 4 to 6, hence a higher cation mobility is observed for lay-
ered V$_2$O$_5$ than for spinel Mn$_2$O$_4$ (Figure 13a,c). This prediction
is consistent with the high cation mobilities observed in layered
V$_2$O$_5$–based electrode materials for ZIABs and AIABs.[57,119]

Based on these energetics arguments, Rong et al. therefore
suggested two design rules to improve MV-cation mobilities:
1) Design crystal structures with no pre-existing MV-ion occu-
pancies in the pristine synthesized state (as adding MV ions
into the designed host during high-temperature synthesis
was argued to likely push them into the lowest-energy anion-
coordination environments). Indeed, this strategy is being
increasingly adopted for vanadium-based and manganese-
based ZIAB cathodes with relative success.[33–59] 2) Design
crystal structures with ion-migration pathways wherein the
mobile cation undergoes minimal changes in anion-coordi-
nation geometries between stable states, transitory states,
and intermediate states. However, Rong et al.’s predictions are
constrained to ideal cases which neglect electrolyte effects.
For example, both the strong solvation interactions between
the cation and the solvent, and the presence of crystal water
in host lattice, can alter cation-insertion behaviors quite
dramatically.[51,100]

Another approach to improve MV-cation mobility is by
reducing the electrostatic repulsions between MV ion and
the transition metal centers inside the host lattice. One way
to achieve such reduced electrostatic interactions is to create
transition-metal vacancies in the host, as discussed in Section
2.1.1 (discussion for λ-MnO$_2$). Transition-metal vacancies can
be introduced into the crystal structure via two methods: 1) by
modifying atmospheric conditions or solution-matrix condi-
tions during syntheses,[150] e.g., Sánchez and Pereira-Ramos
saturated a sol–gel mixture with CO$_2$ ultimately producing a
Mn-vacancy-rich spinel (Mn$_{2.15}$Co$_{0.37}$O$_4$) which demonstrated
reversible intercalation of Mg$^{2+}$ unlike the stoichiometric com-
 pound which was irreversible;[151] 2) by partial substitution
of transition-metal sites by supervalent elements,[152,153] e.g.,
Hahn et al. achieved 0.91 vacancies per formula unit of γ-Fe$_2$O$_3$
via Mo$^{6+}$ doping on Fe sites.[154]

On the other hand, replacing the oxide sublattice with a
sulfide sublattice typically induces better ion mobilities.[155–157] This
is due to two factors: 1) a diffuse electron cloud in the
anionic sublattice which facilitates weaker electrostatic interac-
tions with the mobile cation, 2) a bigger anionic radius which
enlarges openings in the host structure for intercalation. How-
ever, using a chalcogenide framework may also reduce the inter-
calation potential as demonstrated in a Mo$_6$S$_8$–based ZIAB.[119]

4.1.2. Dissolution of Redox-Active Transition-Metal Centers
from Electrodes

Electrode performances can degrade if the transition-metal
elements forming the redox-active centers of intercalation
materials dissolve in aqueous electrolytes. This has been observed to occur in ZIAB and AIAB electrodes containing vanadium\(^{[50,54,59,145]}\) and manganese.\(^{[42,43]}\) Normally, while interacting with water molecules, transition-metal elements will exhibit different stable phases depending on both the pH and the applied potential. This information is summarized in what is known as an \(E\text{–}pH\) or Pourbaix diagram, for example, Figure 14a,b for manganese and vanadium.\(^{[158,159]}\)

Manganese and vanadium are relatively common elements being explored for use in ZIAB cathodes and AIAB cathodes. They can exist in various phases in water solution: \(\text{MnO}_2\)(s), \(\text{Mn}^{2+}\text{(aq)}, \text{MnO}_4^-\text{(aq)}, \text{Mn}_2\text{O}_4\text{(s)}, \text{Mn(OH)}_2\text{(s)}, \text{HMnO}_2^-\text{(aq)},\) and \(\text{Mn}\text{(s)}\) for manganese and \(\text{VO}_2^+\text{(aq)}, \text{V}_2\text{O}_5\text{(s)}, \text{V}_3^+\text{(aq), V}_2\text{O}_7^-\text{(aq), V}_2\text{O}_3\text{(s)}, \text{V}_2\text{O}_4\text{(s), H}_3\text{V}_2\text{O}_7^-\text{(aq), VO}_4^-\text{(aq), H}_2\text{VO}_4^-\text{(aq), VO}_2^-\text{(aq), and V}_2\text{O}_5\text{(s)}\) for vanadium. During operation, when \(\text{MnO}_2\) cathodes cycle between 0 and 1.2 V (vs saturated calomel electrode (SCE)) at a mildly acidic pH, a thermodynamic driving force exists to reduce solid \(\text{MnO}_2\) to aqueous \(\text{Mn}^{2+}\) according to the Pourbaix diagram. Only at applied potentials higher than 1.2 V (vs SCE) will manganese be stable as \(\text{MnO}_2\), as observed experimentally.\(^{[39,48]}\) On the other hand, when vanadium-based cathodes are cycled between 0 and 0.6 V (vs SCE) in ZIABs at mildly acidic conditions, the stable vanadium phase is not solid \(\text{V}_2\text{O}_5\), but aqueous \(\text{VO}_2^+\).\(^{[114]}\)

Here, it is important to realize that the dynamic transformations between solid and aqueous phases of a transition metal are not necessarily reversible. This may cause a failure in structural integrity and “orphaned” active masses which are cut off from the electrical network of the electrode, as also observed experimentally.\(^{[39]}\) Indeed, the dissolution of transition-metal redox-active centers in an electrode must be controlled and minimized by optimizing battery operating conditions: the

![Figure 14. Pourbaix diagram of a) manganese and b) vanadium in water. Reproduced with permission.\(^{[158]}\) Copyright 2018, RSC. c) Charge/discharge cycling of the LiTi\(_2\)(PO\(_4\))\(_3\)/LiFePO\(_4\) aqueous lithium-ion battery in 1 M Li\(_2\)SO\(_4\) + 0.1 M LiOH (“1” with O\(_2\) at 6 C, “2” without O\(_2\) at C/8, and “3” without O\(_2\) at 6 C). d) The typical self-discharge curves of LiTi\(_2\)(PO\(_4\))\(_3\) in 1 M Li\(_2\)SO\(_4\) + 0.1 M LiOH at pH 13, i) with O\(_2\) and ii) without O\(_2\). Reproduced with permission.\(^{[160]}\) Copyright 2010, Springer Nature. Cyclic voltammogram profiles of LiFePO\(_4\) for 50 cycles, at a scan rate of 5 mV s\(^{-1}\) at various operating conditions in 0.5 M Li\(_2\)SO\(_4\): e) at pH 7 without O\(_2\); f) at pH 7 with O\(_2\); g) at pH 7 in the solution with O\(_2\) bubbled for 2 h. Reproduced with permission.\(^{[161]}\) Copyright 2010, Elsevier Ltd.](image-url)
potential limits for electrode charging and discharging, and the electrolyte pH.

4.1.3. Electrode Reactions with Dissolved O$_2$ in the Electrolyte

The presence of dissolved oxygen in aqueous battery systems has been shown to be damaging to electrochemical cycling performances by Luo et al.$^{[160]}$ They made the point by showing a drastic improvement in cycling stability (Figure 14c) and shelf life (Figure 14d) of Li$_{1-x}$Ti$_2$(PO$_4$)$_3$-cathode batteries using a hermetic Ar-purged electrolyte. By Ar-gas purging, the stability of the open-circuit potential open-circuit voltage (OCV) was extended from just 15 h in an oxygen-containing electrolyte. Besides Ar purging, N$_2$ purging of the electrolyte has also resulted in similar improvements for LiFePO$_4$ in a 0.5 m Li$_2$SO$_4$ electrolyte.$^{[161]}$ In gas-purged electrolyte, the LiFePO$_4$ CV curves showed relatively stable reversible peak intensities for 50 cycles (Figure 14e), unlike the performance in electrolyte with dissolved O$_2$ (Figure 14f,g).

In both the reports, the authors argued that O$_2$-driven oxidation of charged electrodes (a parasitic reaction) directly contributes to rapid OCV deterioration and strong capacity fading. At present, the use of inert-gas purging for electrolytes is gaining popularity for ZIAB and AIAB assembly.$^{[60,139,145]}$

4.1.4. Anodic-Potential Stability Limits for Zn$^{2+}$-Intercalated and Al$^{3+}$-Intercalated Host Materials

Aqueous electrolytes are typically less stable than nonaqueous electrolytes from an electrochemical standpoint. This is because water has a thermodynamic oxidation potential and a thermodynamic reduction potential which differ by a narrow 1.23 V. This limited voltage window often means that water electrolysis may occur when water is placed in direct contact with materials containing metallic elements, either readily at rest or with an externally applied bias. Where equilibria between dissolved H$^+$, OH$^-$, O$_2$, H$_2$, and H$_2$O (the principal ionic/molecular species involved in water electrolysis reactions), and the host materials supporting intercalated metal ions (M = Li/Zn/Al) are concerned, a Nernst equation can be setup to deduce thermodynamic trends.

The introduction of more positive charges into a host material during cation intercalation is possible due to charge compensation in the oxidation state of a redox-active center (typically a transition metal), while maintaining the integrity of the lattice structure. With more cations intercalated, the host material undergoes electrochemical reduction. This implies that a fully intercalated host material exists at a minimum reduction potential, which represents its stability limit in the negative-potential direction. Forcing current beyond this anodic potential limit may induce redox coupling directly between the intercalated host material and H$_2$O. The following reaction can occur in O$_2$-free water

\[
M\text{(intercalated)}+ (x)\text{H}_2\text{O} \Leftrightarrow M^{x+}+(x)\text{OH}^- + \left(\frac{x}{2}\right)\text{H}_2 \quad (5)
\]

This equilibrium exists at a potential $V_M$. In theory, an electrode potential higher than $V_M$ would drive this reaction backward. Whereas, an electrode potential lower than $V_M$ would drive this reaction forward which may lead to destabilization of the cation-intercalated host material. That is, under an applied bias potentially shifting toward the negative voltage direction, the host material undergoes reduction until reaching $V_M$. At potentials below $V_M$, three reactions occur simultaneously when the cation-intercalated host is in contact with water: 1) the host material loses electrons to water and oxidizes, 2) water accepts electrons to reduce to hydrogen, and 3) intercalated cations deintercalate. Therefore, only above $V_M$ would cations exist in a stable state within the host material.

On the other hand, the following reaction becomes dominant in the presence of dissolved O$_2$

\[
M\text{(intercalated)} + \left(\frac{x}{4}\right)\text{O}_2 + \left(\frac{x}{2}\right)\text{H}_2\text{O} \Leftrightarrow M^{x+}+(x)\text{OH}^- \quad (6)
\]

Because O$_2$ is a highly oxidizing substance, dissolved O$_2$ in H$_2$O can significantly shift $V_M$ toward higher values. Based on the argument above, equilibrium at a lower $V_M$ is favorable for stabilizing intercalation host materials, while equilibrium at a higher $V_M$ renders electrodes to be progressively unstable in an aqueous battery system. Hence, lower values of $V_M$ increase the choices for intercalation host materials for electrodes in aqueous battery systems.

In this section, we derive $V_{Li}$, $V_{Zn}$, and $V_{Al}$ parameters in the presence and in the absence of dissolved O$_2$, using an approach similar to Li et al. and Luo et al.$^{[115,160]}$ Assume we have been given an intercalation compound which contains intercalated metal-ion species (Li/Zn/Al), and which exists at a chemical potential of $\mu_M$. Presumably, little bubbles of O$_2$/H$_2$ will form over the surface of the inserted host material, such that any gas will be at a pressure of approximately 1 atm (standard state conditions). Therefore in equilibrium:

\[
\mu^\text{int}_M + \frac{x}{4} \mu^\text{int}_0 + \frac{x}{2} \mu^\text{int}_{H_2O} = \mu_M^{x+} + x\mu_{\text{OH}^-} \quad (7)
\]

In absence of O$_2$

\[
\mu^\text{int}_M + x\mu^\text{int}_{H_2O} = \mu_M^{x+} + x\mu_{\text{OH}^-} + \frac{x}{2} \mu^\text{int}_{H_2} \quad (8)
\]

where $\mu_M^{x+}$ and $\mu_{\text{OH}^-}$ are the chemical potentials of M$^{x+}$ and OH$^-$ in solution, respectively, and $\mu^\text{int}_0$, $\mu^\text{int}_{H_2O}$, and $\mu^\text{int}_{H_2}$ are the chemical potentials of O$_2$, H$_2$, and H$_2$O in their standard states, respectively. The chemical potentials of OH$^-$ and M$^{x+}$ in solution can be related to concentration values using the Nernst equation

\[
\mu_M^{x+} = \mu^\text{int}_{M^{x+}} + \frac{kT}{xe} \ln [M^{x+}] \quad (9)
\]

\[
\mu_{\text{OH}^-} = \mu^\text{int}_{\text{OH}^-} + kT \ln [\text{OH}^-] \quad (10)
\]

where $\mu^\text{int}_{M^{x+}}$ and $\mu^\text{int}_{\text{OH}^-}$ are the chemical potentials of the metal ions and hydroxyl ions, respectively, both in 1 m solution; $k$ is Boltzmann’s constant and $T$ is temperature in Kelvin units.
Following McKinnon and Haering,[162] $V_M$ can also be calculated with the following equation

$$V_M = -\frac{1}{ne} (\mu_M - \mu_M^0)$$  \hspace{1cm} (11)

where $\mu_M^0$ is the chemical potential of the metal-ion in metal and $n$ is the number of electrons transferred with magnitude of electron charge, $e$. Based on Equations (7)–(11) and substituting standard thermodynamic data from the tables “Thermodynamic properties of aqueous ions” and “Standard thermodynamic properties of chemical substances” in the CRC handbook,[163] the following equations can be derived:

In presence of $O_2$

$$V_{Li} = 4.268 - 0.059pH - 0.0591 \log[Li^+] \hspace{1cm} (vs \ Li^+/Li)$$  \hspace{1cm} (12)

In absence of $O_2$

$$V_{Li} = 3.039 - 0.059pH - 0.0591 \log[Li^+] \hspace{1cm} (vs \ Li^+/Li)$$  \hspace{1cm} (13)

In presence of $O_2$

$$V_{Zn} = 4.273 - 0.059pH - 0.0148 \log[Zn^{2+}] \hspace{1cm} (vs \ Li^+/Li)$$  \hspace{1cm} (14)

In absence of $O_2$

$$V_{Zn} = 3.045 - 0.059pH - 0.0148 \log[Zn^{2+}] \hspace{1cm} (vs \ Li^+/Li)$$  \hspace{1cm} (15)

In presence of $O_2$

$$V_{Al} = 4.290 - 0.059pH - 0.0066 \log[Al^{3+}] \hspace{1cm} (vs \ Li^+/Li)$$  \hspace{1cm} (16)

In absence of $O_2$

$$V_{Al} = 3.061 - 0.059pH - 0.0066 \log[Al^{3+}] \hspace{1cm} (vs \ Li^+/Li)$$  \hspace{1cm} (17)

Equations (12)–(17) (plotted in Figure 15) indicate that $V_M$ is a function of three parameters, namely, the intercalating metal-ion concentration in the electrolyte (as determined by electrolyte salt concentration), electrolyte pH, and dissolved $O_2$. With increasing salt concentration, $V_M$ decreases marginally by at most 0.15 V beginning steeply at the dilute limit to a flat line at the higher concentrations. Interestingly, the concentration dependence of $V_M$ is stronger for the case of Li as compared to Zn and Al. $V_M$ shows a stronger dependence on pH, varying by a difference as large as 0.7 V (from pH values between 1 and 14). An $O_2$-free environment shifts $V_M$ to more negative potentials (panels a–c against panels d–f), causing a shift as large as 1.25 V for a given pH. Based on these trends, we speculate that concentrated, $O_2$-free electrolytes with high pH values are better for low-voltage insertion electrodes.

We also note that since kinetic effects and additional side reactions have been neglected during this derivation, the applicability of these equations is limited and some anomaly is expected. For example, 1) He et al. observed capacity fading for LiFePO4 in an increased pH of electrolyte, wherein the transition metal center reacted with OH−.[161] 2) Tian and Yuan measured cycling stability for the LiMn2O4 cathode in varying LiNO3 electrolyte concentration.[164] Cyclic stability first increased and then decreased when the electrolyte concentration was changed.

---

**Figure 15.** Equilibrium voltage, $V_M$, as a function of $Li^+/Zn^{2+}/Al^{3+}$ concentration in electrolyte, in the presence of dissolved $O_2$ with pH values of a) 1, b) 7, and c) 14; and in the absence of dissolved $O_2$ with pH values of d) 1, e) 7, f) 14. Solid lines represent the equilibrium equations while shaded area represents different regions where Li/Zn/Al inserted electrodes are stable/unstable.
from 1 to 5 m and then 9 m. This anomaly can be due to Mn$^{2+}$ dissolution, not accounted for in our derivation. Tian and Yuan reported a pH of ≈5.5 for all the electrolytes where manganese can dissolve into the electrolyte as predicted by the Pourbaix diagram in Figure 14b.

### 4.1.5. Effect of Doping on Cycling Stability

Cycling stability is a major challenge in many of the electrodes studied for ZIABs\cite{37,43,44,48,50} and AIABs.\cite{137,138,145} Doping the transition-metal sites in the crystal structure with other elements can mitigate this issue as demonstrated previously.\cite{165,166} Yuan et al.\cite{165} showed that for aqueous lithium batteries, doping manganese in LiMn$_2$O$_4$-spinel cathode with 0.1 mol Al can stabilize its octahedral site and also reduce the Jahn–Teller distortions (Figure 16a). A similar effect was observed for nonaqueous Zn-ion batteries where structural stability in ZnCo$_2$O$_4$ spinels was improved by Al doping.\cite{167} For ZIABs, Jo et al. demonstrated improved structural stability and cycling performance by Al doping in Hollandite-type (isostructural to α-MnO$_2$) VO$_{1.52}$(OH)$_{0.77}$, as shown in Figure 16b.\cite{168} The improved cycling stability was ascribed to the formation of Al–O bonds which are more stable than V–O bonds, as indicated by the formation energies of Al$_2$O$_3$ (−1573 kJ mol$^{-1}$) and V$_2$O$_5$ (−1139.3 kJ mol$^{-1}$).\cite{163}

### 4.1.6. Proton/Hydronium Coinsertion

One common phenomenon observed with using an acidic aqueous electrolyte in ZIAB and AIAB electrodes is the parallel insertion of protons or hydronium (H$_3$O$^+$) species along with metal cations.\cite{42,47,85,139} Sun et al. used electrolytic manganese dioxide (EMD–MnO$_2$) to demonstrate H$^+$ coinsertion with Zn$^{2+}$ during discharging.\cite{47} Two distinct discharge plateaus were observed with the contribution from region II becoming insubstantial at high cycling rates (Figure 16c). The galvanostatic intermittent titration technique profile during discharging also showed two separate regions (Figure 16d) with much higher charge transfer resistance and diffusion resistance in region II. They ascribed these observations to different ionic species inserting in and speculated that small sized H$^+$ inserts before Zn$^{2+}$. To further prove this point, the same cell was discharged in a MnSO$_4$ electrolyte first, and then in a mixed ZnSO$_4$ + MnSO$_4$ electrolyte. The cell in the Zn$^{2+}$ ion containing electrolyte showed two plateaus in the voltage profile during discharge, whereas the cell in the electrolyte without Zn$^{2+}$ ion had only one sloping plateau, indicating that only H$^+$ inserts in the latter case (Figure 16e). Additionally, the formation of MnOOH phase preceded ZnMn$_2$O$_4$ while discharging, indicating that H$^+$ inserts before Zn$^{2+}$.

Apparently, this phenomenon is highly system-dependent. While Sun et al.’s study showed that the capacity contributions due to protons inserting into MnO$_2$ can be as high as...
≈130 mAh g\(^{-1}\), the capacity contributions due to any proton-insertion mechanism into V\(_3\)O\(_7\).H\(_2\)O was found to be negligible.\(^{[102]}\) A lack of proper control of proton/hydronium insertion can lead to fluctuations in the capacities observed. In other aqueous MV-ion systems, researchers have demonstrated that H\(_3\)O\(^+\) intercalation can compete with metal-cation intercalation,\(^{[169]}\) which might explain the dependence of capacity on increasing H\(_3\)O\(^+\) concentration in organic electrolytes.\(^{[89,116]}\) Additionally, as Gu et al. have speculated, a high number of protons in the host may increase the diffusion barrier for intercalating cations and subsequently block intercalation channels.\(^{[170]}\)

Three strategies can be adopted to reduce proton/hydronium coinsertion: 1) increasing the electrolyte pH,\(^{[160]}\) 2) using supersaturated salt solutions, 3) choosing appropriate crystal structures for the host, as the protonation has been shown to be dependent on the host crystal structure.\(^{[171,172]}\) Crystal structures showing higher lattice distortion during proton insertion will be least accommodating to H\(^+\). Experimental observations and first-principle calculations for well-known lithium structures have shown that protonation is favorable generally according to the following order: layered > spinel > olivine.\(^{[171,172]}\)

### 4.2. Electrode–Electrolyte Interface Formation

The initial step of electrolyte degradation and subsequent formation of a solid electrolyte interface (SEI) at the anode or a cathode–electrolyte Interface (CEI) at the cathode in a newly assembled battery enables cycling in nonaqueous Li-ion batteries. It leads to the formation of a stable, ionically conductive, and electronically insulating layer which stabilizes the electrode–electrolyte interfaces (EEIs). Unfortunately, the direct decomposition products of water in an aqueous electrolyte system are either volatile gases or soluble ions.\(^{[158]}\) Lack of solid EEIs can lead to unchecked oxygen/hydrogen evolution at the electrode surfaces, and a narrow voltage-operating window. The lack of EEI also allows the cointercalation of water molecules with MV ions, (Figure 17a,b) and this can lead to degradation of the host-material lattice structure.\(^{[139]}\) As demonstrated in aqueous lithium-ion battery systems, researchers have tried to overcome this problem by depositing an artificial solid layer on the electrode,\(^{[173]}\) adding additives to the electrolyte,\(^{[174,175]}\) and by using concentrated electrolytes.\(^{[175–177]}\)

#### 4.2.1. Effect of Artificial Layer on the Electrode

Zhi et al. reported substantially enhanced cycling stability for LiMn\(_2\)O\(_4\) cathodes in aqueous electrolyte (1 m Li\(_2\)SO\(_4\) + 2 m ZnSO\(_4\)) by coating graphene layers on LiMn\(_2\)O\(_4\) particles, effectively using graphene films as an artificial CEI.\(^{[173]}\) They proposed that Li\(^+\) can diffuse in two ways in graphene layers: 1) parallel to the graphene layers, 2) perpendicular to the
graphene layer when structural defects were present. Based on this, Zhi et al. proposed permeation-based mechanisms for LiMn$_2$O$_4$ cathode without and with graphene coating (Figure 17c,d). Unlike the uncoated cathode, graphene-coated cathodes showed limited diffusivity for Li$^+$ into LiMn$_2$O$_4$ because of limited permeation of graphene layers. Zhi et al. speculate that this leads to a suppressed Jahn–Teller distortion of LiMn$_2$O$_4$ which resulted in enhanced cycling stability.

Similarly, Son et al. reported the use of a polymeric film composed of thermal-cyclized polyacrylonitrile and Mg trifluoromethanesulfonate as an artificial EEI interphase which could conduct Mg$^{2+}$ ion, making it possible to reversibly electrodeposit and strip Mg in a water-based electrolyte.\cite{Suo2019} The polymer-coated Mg and uncoated Mg were comparatively studied as anodes in full cells (anode/V$_2$O$_5$) in 0.5 m magnesium bis(trifluoromethanesulfonyl) imide/propylene carbonate (PC)+ 3 m H$_2$O. The coated Mg anode showed a slight decrease in capacity over 40 cycles, whereas the capacity for a cell with uncoated Mg metal anode dropped to zero within 8 cycles. This study might open avenues for AI metal to be used as the anode in aqueous electrolytes.

4.2.2. Effect of Supersaturated Electrolyte

Suo et al. explored SEI layer formation in a highly concentrated (21 m “water-in-salt” (WIS)–LiTFSI-based electrolyte.\cite{Suo2019} Based on differential electrochemical mass spectrometry results, they observed suppressed hydrogen and oxygen evolution in 21 m electrolyte, indicating the formation of an SEI layer which helped in suppressing water decomposition. A preferential reduction of salt anions over water electrolysis was speculated to be responsible for the formation of a favorable battery SEI. Using time-of-flight secondary ion mass spectrometry (TOF-SIMS), Suo et al. showed the dominant presence of F$^-$ ions which could have formed by reduction of anionic complexes. XPS and soft-X-ray absorption spectra (sXAS) revealed the presence of Li$_2$CO$_3$ and Li$_2$O which could have formed by reduction of anionic complexes. Using time-of-flight secondary ion mass spectrometry (TOF-SIMS), Suo et al. showed the dominant presence of F$^-$ ions which could have formed by reduction of anionic complexes. XPS and soft-X-ray absorption spectra (sXAS) revealed the presence of Li$_2$CO$_3$ and Li$_2$O which could have formed by reduction of anionic complexes.

It has been hypothesized that unlike the case of superconcentrated electrolyte, in diluted aqueous electrolytes, the reduction products can quickly hydrolyze and dissolve, and thus be unable to form stable SEI. Suo et al. argued, even if a SEI formed in the initial cycles, chances are it would dissolve over repeated charge/discharge cycling. Therefore, superconcentration of an electrolyte may play a critical role in not only forming SEI but also keeping it intact over long charge/discharge cycles.

In another work of their group, Suo et al. made a more efficient SEI layer by introducing the concept of “water-in-bisalt (WIBS)”, where a mixed molten-salt system (21 m lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and 7 m lithium trifluoromethane sulfonate (LiOTf)) forms a more concentrated electrolyte as compared to WIS.\cite{Suo2019} The hydrogen evolution potential and concomitant current ascribed to H$_2$ evolution decreased significantly in WIBS (from 1.9 to 1.83 V (vs Li/Li$^+$) and from 10 to 4 mA cm$^{-2}$ in WIS and WIBS, respectively). The importance of a protective coating is illustrated in Figure 18a, wherein the cycling stability of the electrode is improved with carbon coating and by the introduction of LiOTf in WIS. Interestingly, in WIBS, a more responsive SEI formed as was indicated by a rapid rise in Coulombic efficiency (99% in 40 cycles and 97% in 60 cycles for WIBS and WIS, respectively) (Figure 18b). Suppressed H$_2$ evolution, as a result of this outstanding SEI, enabled the use of a low potential electrode (carbon-coated TiO$_2$) paired with LiMn$_2$O$_4$ to yield an unprecedented discharge voltage (2.1 V) and energy density (100 Wh kg$^{-1}$). Suo et al. attributed the stable SEI formation to an increased cation/water ratio of 0.5:1 in WIBS as compared to 0.38:1 in WIS.

It is worth mentioning here that TFSI salts of Zn and Al may show limited solubility in water.\cite{Suo2019} Therefore alternative electrolyte formulations may need to be explored which can deliver the advantages of supersaturation.

4.2.3. Effect of Electrolyte Additive

Stojković et al. for the first time demonstrated the successful use of an additive to enhance the behavior of Li intercalation in an aqueous solution.\cite{Stojkovic2019} An improved capacity and cycling stability was observed for Li$_{1.05}$Cr$_{0.10}$Mn$_{1.85}$O$_4$ by adding 1 wt% vinylene carbonate (VC) in a saturated aqueous solution of LiNO$_3$. Based on the positive influence of VC in aqueous solution, Stojković et al. suggested that VC enables the formation of a protective film on the electrode that prevents the progressive penetration of water into electrode materials, detrimental to Li-ion intercalation.

On similar lines, Wang et al. explored the role of tris(trimethylsilyl) borate (TMSB) in 21 m LiTFSI aqueous electrolyte which leads to the formation of a CEI.\cite{Wang2019} First-principle calculations showed that the highest occupied molecular orbital (HOMO) level of TMSB was higher as compared to that of water and salt anions in WIS (Figure 18c). This allowed for preferential oxidation of TMSB and the subsequent formation of silicon-based and boron-based compounds which could form CEI (Figure 18d). The CEI on the electrode was studied using TEM for a LiCoO$_2$–Mo$_6$S$_8$ full cell. For LiCoO$_2$ electrode cycled in TMSB-added electrolyte, Wang et al. detected a thin amorphous layer, supposedly CEI (shown in red, Figure 18e). Also, as compared to LiCoO$_2$ electrode cycled in the electrolyte without TMSB (Figure 18f), LiCoO$_2$ electrode cycled in the presence of TMSB showed a relatively intact surface without evident surface defects (Figure 18e). CEI formation also suppressed Co dissolution, as indicated in inductively coupled plasma - optical emission spectrometry (ICP-OES) analysis of cycled electrolytes. This enabled a long life of 1000 stable charge/discharge cycles for the LiCoO$_2$–Mo$_6$S$_8$ full cell.

4.3. Current Collector

4.3.1. H$_2$ Evolution

Hydrogen evolution is strongly dependent on the operational voltage range for cycling, the electrolyte formulation, and the current collector used.\cite{Stojkovic2019, Son2019, Wang2019} The limited electrochemical stability of water places restrictions on what electrodes can be used in aqueous batteries. Using a Pourbaix diagram, we can design electrolytes with appropriate pH values to minimize H$_2$ and O$_2$ evolution.\cite{Stojkovic2019} Alternatively, a highly concentrated electrolyte
can give an expanded voltage range of 3 V, as demonstrated by Suo et al.\cite{181} Though the effect of electrolyte pH and concentration has been discussed widely,\cite{10,158,182,183} the role of the current collector in H\textsubscript{2}/O\textsubscript{2} evolution is often overlooked, and here in this work, will be discussed in this section.

Recently, Lahan and Das demonstrated the importance of choosing an appropriate current collector for aqueous systems in order to suppress H\textsubscript{2} evolution.\cite{184} Lahan and Das examined how Al insertion in TiO\textsubscript{2} samples varied when they were coated on different current collectors (stainless steel, graphene, titanium, and nickel). Indeed, they observed different extents of electrochemical activity for Al insertion, and it was speculated that the TiO\textsubscript{2} sample coated on a graphene current collector significantly suppressed H\textsubscript{2} evolution and allowed for Al\textsuperscript{3+} intercalation.

How favorably hydrogen is evolved from the interaction of water and a current collector specie can be predicted using Figure 19a, which shows the strength of adsorbed metal–hydrogen (M–H) bonds.\cite{127,128} With increasing M–H bond strength, the exchange current for H\textsubscript{2} evolution rises to a maximum and then reduces again, forming a volcano-shaped curve (Figure 19a). To the left of this maximum, the propensity for H\textsubscript{2} evolution remains low as H bonds weakly with the surface. However, on the right side of the maximum, this bonding becomes so strong that available sites for H\textsuperscript{+}H recombination are decreased, again reducing the exchange current density.\cite{127,128} To illustrate: 1) Zn falls on the left of the maximum, thus suppressing H\textsubscript{2} evolution to an extent and allowing for Zn metal as anode in ZIBs, 2) Ti falls on the extreme right of curve and shows reduced H\textsubscript{2} evolution as also observed by Lahan and Das; and Adams and Kundu,\cite{133,185} 3) Pt sits at the curve maximum and shows minimum suppression for H\textsubscript{2} evolution.

Therefore, elements on either extremes of this volcanic curve are suggested to be preferred current collectors for electrodes cycled at potentials close to the H\textsubscript{2}-evolution potential in aqueous batteries. On the other hand, elements at the maximum of the M–H curve are suited for electrolyte studies.
where kinetic overpotential is a minimum on the current collector surface.

4.3.2. Corrosion

Conventional Cu and Al current collectors can corrode in acidic electrolytes, both in ZIABs and AIABs. Currently, Ti and stainless steel are popular current collectors for ZIABs, although better substitutes are being explored. On the other hand, for AIABs (Table 5), whereas stainless steel corrodes strongly in highly concentrated electrolytes of Al salts,\textsuperscript{[132]} Pt, Ti, and Ni are expected to show adequate corrosion resistance,\textsuperscript{[159]} but are expensive.\textsuperscript{[186]} As an alternative to the aforementioned current collectors, Gheytani et al. tested chromate conversion–coated aluminum foil in a 2.5 M Li$_2$SO$_4$ and showed comparable performance to titanium foil (Figure 19b).\textsuperscript{[186]} Significant corrosion was observed for an uncoated Al current collector as compared to a coated one which showed stable capacity over 50 cycles (Figure 19c).

Another way of avoiding corrosion is to completely cover all the sides of a current collector such that current collector–electrolyte contact is minimized. This can be done by 1) completely coating the current collector by active material on all sides and 2) covering the bare current collector area with unreactive coatings. For example, Liu et al. coated epoxy resin on the edges and on the rears of titanium foil to avoid the corrosion.\textsuperscript{[123]}

Overall, the choice of current collector material seems trivial, but is crucial to avoid unwanted hydrogen evolution and corrosion effects.

5. Summary

A battery system which has a Zn/Al metallic anode paired with a high-capacity cathode material in an aqueous electrolyte might fit the criteria for BESS, provided the system has a long cycle life. Metallic Zn anodes have been successfully cycled in mildly acidic aqueous electrolytes,\textsuperscript{[45,76]} but not metallic Al anodes, fundamentally due to an electrochemical plating/stripping voltage occurring too far from the stable potential window of water. Nonetheless, advancements in widening the electrochemical stability window of aqueous electrolytes,\textsuperscript{[175,177,181]} and the usage of protective interphases,\textsuperscript{[178]} might allow the use of Al metal as an anode in the near future.
In terms of cathode materials, various host structures have demonstrated electrochemical activity for Zn and/or Al. Among these, manganese oxide full cell ZIABs have realized competitive energy densities: 158.5 Wh kg\(^{-1}\) for \(\beta\)-MnO\(_2\)\(^{[39]}\) and 170 Wh kg\(^{-1}\) for \(\alpha\)-MnO\(_2\)\(^{[42]}\) as compared to other water-based competing systems such as aqueous Li batteries (50–200 Wh kg\(^{-1}\))\(^{[160,181,187,188]}\) aqueous Na-ion batteries (~100 Wh kg\(^{-1}\))\(^{[10]}\) lead–acid (30–50 Wh kg\(^{-1}\)), and vanadium redox-flow batteries (10–30 Wh kg\(^{-1}\))\(^{[189]}\) Recent reports also suggest that energy densities of ~105 Wh kg\(^{-1}\) can be achieved in full-cell AIABs if TiO\(_2\) (anode) and Na\(_3\)V\(_2\)(PO\(_4\))\(_3\) (cathode) are used\(^{[126,145]}\).

Comparison of ZIAB cathodes against conventional nonaqueous Li-ion battery cathodes reveals that the energy and power densities of ZIAB cathodes can be on par with their Li-ion counterparts (Figure 20). While some of the best Li-ion cathodes materials, Li(TM)O\(_2\) (TM = Ni, Co, Mn), can deliver an energy density of ~120–160 Wh kg\(^{-1}\) and power density of 200–300 W kg\(^{-1}\)\(^{[38]}\) \(\beta\)-MnO\(_2\) as ZIAB cathode has been demonstrated to feasibly enable energy densities of ~100–200 Wh kg\(^{-1}\) and power densities of 100–10 000 W kg\(^{-1}\)\(^{[160]}\) In the case of AIAB cathodes, Na\(_3\)V\(_2\)(PO\(_4\))\(_3\) when used against TiO\(_2\) anode can deliver a high energy density of ~150 Wh kg\(^{-1}\) and power densities as high as ~1400 W kg\(^{-1}\)\(^{[126,145]}\). Specifically, high power densities demonstrated by ZIABs and AIABs are attractive for grid level energy storage as energy demand in common households rapidly rise during the evenings and draw much power from the grid, coincidentally when solar-dependent renewables cannot produce energy.

However, most reports on ZIAB and AIAB electrode materials show ordinary electrochemical performance, owing to various challenges highlighted in this review. Solving these problems requires intricate battery engineering, controlling design parameters involving the active material, electrolyte, and current collector together (Figure 21). Here, it is important to note that adjusting one parameter may cause untoward effects on other parameters, ultimately causing inefficiencies in the overall battery performance. Therefore, at the cell level, BESS battery components must be optimized in unison, and not individually.

6. Future Outlook

One of the most essential nuances in electrochemistry between aqueous batteries and nonaqueous batteries is the role of water during cation insertion in electrode materials. This applies not only for ZIABs and AIABs, but in general to all aqueous MV-ion batteries.

Water comes into play in three cases: 1) within the crystal structure of the electrode active material (or crystal water); 2) as part of the hydration sphere of the intercalating cation; 3) at the electrode surface as chemisorbed H\(_2\)O molecules.

It is possible for crystal water introduced into intercalation host materials during synthesis or cell operation to be beneficial in three ways, by: 1) enlarging ion tunnels or layers in the crystallographic lattice to allow more facile cation insertion (Figure 22a),\(^{[51,148]}\) 2) providing structural support to the lattice...
framework for stable repeated (de)intercalation,[19,51,190] and 3) providing electrostatic shielding for intercalating cations to weaken cation–anion bonds along the migration pathway.[95,98]

However, water is often tightly bound to aqueous MV ions in the form of a hydration sphere.[100,191–193] Thus, hydrated cations may interact with a crystalline host structure in different ways, depending strongly on size considerations.[100] When the ion-channel size is sufficiently large to accommodate the hydrated cation, desolvation may be not necessary for successful cation intercalation (Figure 22b). When the ion-channel size is relatively small, partial desolvation phenomena might occur (Figure 22c).

Further, water may drive specific reactions at the electrolyte–electrode interface. It has been speculated that the electrode–electrolyte interface can be rich in “dangling bonds.”[194] These dangling bonds arise from edge terminations of the repeating lattice of a crystalline active material, and are easily neutralized by chemisorbed H2O molecules.[194] This creates a half-solid and half-liquid coordination environment at the immediate solid–liquid interface, or a “Janus interface.” This Janus interface aids in offsetting energy penalties associated with desolvation of a hydrated cation, hence dramatically easing cation insertion.[102,194]

However, most of these ideas are not well established with direct experimental proofs. We believe understanding these phenomena can yield design guidelines for better electrode/electrolyte materials for aqueous batteries. Thus, experiments tailored to directly investigating the following are recommended to be explored: 1) the dynamic interactions between crystal–water and electrolyte–water during battery operation; 2) mechanisms of MV-ion desolvation at the electrolyte–electrode interface; 3) role of the ion-channel size in crystalline materials for effective intercalation of hydrated MV ions.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

aqueous batteries, cation mobility, electrode dissolution, intercalation, multivalent

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