Progress in rechargeable aqueous zinc- and aluminum-ion battery electrodes : challenges and outlook

Verma, Vivek; Kumar, Sonal; Manalastas, William, Jr.; Satish, Rohit; Srinivasan, Madhavi

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Batteries

V. Verma, S. Kumar, W. Manalastas Jr.,*
R. Satish, M. Srinivasan* 1800111

Progress in Rechargeable Aqueous Zinc- and Aluminum-Ion Battery Electrodes: Challenges and Outlook

Batteries using Zn/Al ions in aqueous electrolytes are highly attractive due to elemental abundance considerations, but attaining reversibility at a high energy density and long-life operation is challenging. Here, recent reports of such batteries are reviewed, focusing on mechanisms of electrochemical activation, electrochemical limitations of aqueous electrolyte and probable solutions/directions are explored which can help in grid level commercialization of Zn-/Al-ion aqueous batteries.

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Progress in Rechargeable Aqueous Zinc- and Aluminum-Ion Battery Electrodes: Challenges and Outlook

Vivek Verma, Sonal Kumar, William Manalastas Jr.,* Rohit Satish, and Madhavi Srinivasan*

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

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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 such as limited cation mobility, spontaneous dissolution, poor cycling, O₂ interaction, untoward proton/hydronium coinser-tion, ineffective electrode–electrolyte interface formation, and current-collector corrosion. We illustrate how these challenges are dependent on some of the battery design parameters, with an aim to find optimized solutions or alternative strategies to increase the viability of Zn-ion aqueous batteries (ZIABs) and Al-ion aqueous batteries (AIABs) in BESS.

2. Aqueous Rechargeable Electrodes for Zn-Ion Storage

In this review, we discuss rechargeable electrodes which can insert Zn²⁺ ions. Since, electrodes for zinc–nickel batteries,^[28,29] alkaline Zn–MnO₂ batteries,^[30,31] or the hybrid zinc aqueous batteries,^[32] store other ions (and not Zn²⁺), we do not discuss these systems here. Majority of 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 Zn²⁺ 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 MnO₆ octahedra either via edge sharing or corner sharing, in multiple ways. Broadly, the polymorphs can be classified into three types of structures, tunnel-type, layered-type, and spinel-type.

Tunnel-type structures (α , β , and γ) are formed by corner-sharing MnO₆ octahedra. The polymorphs differ in terms of tunnel sizes (Figure 2a–c). α -MnO₂ shows a tunnel size of 2 × 2 (wherein 2 × 2 indicates that each side of the tunnel consists of two MnO₆ octahedra); β -MnO₂ has a tunnel size of 1 × 1 and γ -MnO₂ has both 1 × 1 and 1 × 2 tunnels propagating along the same axis. Notably, the tunnels in α -MnO₂ 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 δ -MnO₂ (Figure 2d). Between these sheets, water molecules or other cations can insert, and in the process, further expand the interlayer distance between δ -MnO₂ layers. The presence of one layer of water molecules in between two δ -MnO₂ layers will result in a

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birnessite-type structure (Figure 2f), whereas having two layers of water molecules between two δ -MnO₂ layers creates a buse-rite-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 MnO₆ octahedra can form crystal structures wherein the oxygen sublattice is arranged in cubic-closed packing (CCP). The best example is λ -MnO₂ (or more representatively described by unit cells of Mn₂O₄). Here, the structure is a spinel-type AB₂O₄ (where A = vacancy and B = Mn), and nei-ther tunnels nor layers are formed, as shown in Figure 2e.

2.1.1. Mechanisms of Reversible Zn²⁺ Storage in MnO₂-Based Cathode Materials

A number of mechanisms governing the electrochemistry between Zn²⁺ ions and MnO₂ electrodes have been pro-posed.^[33–48] Although most studies ascribe charge storage to Zn²⁺ intercalation/extraction mechanisms,^[37,39,43,46–48,68,69] other studies suggest conversion mechanisms based on either reversible proton exchange,^[42] or Zn-mediated MnO₂ dissolution/redeposition.^[70]

We also note that most studies on secondary Zn–MnO₂ bat-teries preferentially utilize mildly acidic or neutral electrolytes

Figure 1. a) Typical duck chart showing the imbalances in peak demand and renewable energy production over the course of a day: each line represents the hourly evolution of net load (normal load minus wind and photovoltaics (PV) generation) as sampled on every March 31st of consecutive years. With the yearly increase in PV installations, the spikes in energy production between ≈ 1 and 2 pm grow much more significantly than energy demand (as shown by the dip in the curves). This represents excess energy, and a high risk of overgeneration during afternoons whereas the opposite scenario is expected during late evenings. Data sourced from ref. [2]. b) Comparison of volumetric capacity, cost and abundance parameters of candidate metal anodes for aqueous rechargeable batteries. Data sourced from refs. [24,134,194]

Figure 2. a–e) Various polymorphs of MnO₂. The octahedra represent Mn atoms sitting in oxygen-coordinated environment, in two opposite spin configurations (purple for spin-up and brown for spin-down). Reproduced with permission.^[87] Copyright 2018, ACS. f,g) The Birnessite and buserite structures. MnO₆ octahedra and water molecules are represented by brown polyhedral and white spheres, respectively.

over alkaline electrolytes conventionally used in primary Zn–MnO₂ batteries. Previous attempts in utilizing alkaline electrolytes resulted in poor cycling performances which were attributed to the formation of insulating ZnO at the zinc anode.^[71,72] The high solubility of zinc in alkaline solutions can cause the zinc metal to dissolve as [Zn(OH)₄]^{2–}^[73] and any nonuniformity in [Zn(OH)₄]^{2–} concentration at the zinc metal surface can lead to a nonuniform zinc plating during the charging step, resulting in dendrites.^[74,75] Together, the formation of ZnO phases and zinc dendrites have been suppressed by utilizing mildly acidic electrolytes and a highly reversible electrochemical plating/stripping has been achieved.^[42,76]

α-MnO₂: Xu et al. demonstrated a maximum discharge capacity of 210 mAh g^{–1} for an α-MnO₂/Zn battery in a mildly acidic ZnSO₄ 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 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

Figure 3. a) Cyclic voltammograms for zinc metal (red curve) and α - MnO_2 (blue curve) at 2 mV s^{-1} in aqueous $0.1 \text{ M Zn(NO}_3)_2$ electrolyte. Reproduced with permission.^[45] Copyright 2011, John Wiley and Sons. b) The discharge–charge behavior for α - MnO_2 cathode in i) 1 M ZnSO_4 and ii) electrolyte replaced with fresh 1 M ZnSO_4 electrolyte after 1st discharge. c) Transformation of α - MnO_2 (or cryptomelane) structure into Zn–birnessite via dissolution of Mn^{2+} . White and red spheres represent K^+ and water molecules, respectively. Reproduced with permission.^[48] Copyright 2014, Springer Nature. d) TEM images of α - MnO_2 electrodes discharged to 1 V versus Zn^{2+}/Zn using a mixed electrolyte of $2 \text{ M ZnSO}_4 + 0.1 \text{ M MnSO}_4$. e) STEM-HAADF image showing the elemental distribution in the α - MnO_2 nanorods after the first discharge. Reproduced with permission.^[42] Copyright 2016, Springer Nature.

Anode

(2)

In a separate study, however, Lee et al. deduced a distinct electrochemical insertion mechanism involving H_2O , Zn^{2+} , and α - MnO_2 .^[48] When they indexed TEM diffraction patterns from discharged α - MnO_2 cathodes, they surprisingly found $\text{ZnMn}_3\text{O}_7 \cdot 3\text{H}_2\text{O}$ or Zn–birnessite instead of the expected ZnMn_2O_4 (in the birnessite structure, Zn^{2+} is inserted between a water layer and a MnO_6 layer). Curiously, the Mn^{2+} 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 Mn^{2+} ions present for battery reversibility to occur, and this supported the idea of Mn^{2+} dissolution/deposition being an integral part of the discharge/charge reactions. Lee et al. proposed that discharging α - MnO_2 caused some Mn^{4+} ions forming the tunnel structure to reduce to Mn^{3+} . These Mn^{3+} ions formed later disproportionate to Mn^{4+} and water-soluble Mn^{2+} which dissolves. It is this partial removal of Mn atoms (via Mn^{2+} dissolution) from the lattice that essentially transforms α - MnO_2 to Zn–birnessite. Notably, the two polymorphs are structurally very similar (Figure 3c), and the α - MnO_2 crystal structure can be regenerated later by adding two edge-shared MnO_6 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 Zn^{2+} insertion in α - MnO_2 actually involved a Zn–buserite structure (Zn^{2+} inserted between water and MnO_6 layers in a buserite-type structure), instead of a Zn–birnessite structure.^[69] The crux is that the two- H_2O -layer Zn–buserite structure becomes unstable when the cathode is dried, and thus transforms to one- H_2O -layer Zn–birnessite by losing its extra water layer, explaining their earlier ex situ findings. On a full cycle, the α - MnO_2 structure was therefore proposed to convert to a Zn–buserite structure and back again to the α - MnO_2 structure.

Beyond intercalation-type mechanisms,^[39,43,48,69] Pan et al. proposed a conversion-type mechanism for Zn^{2+} insertion in α - MnO_2 .^[42] The authors showed that micrometer-long α - MnO_2 nanowires transformed into short nanorods and aggregated nanoparticles during the first discharge (Figure 3d). When examined under XRD and TEM, the lattice fringe spacing and diffraction patterns of the discharged nanoparticles and nanorods were indexable to a MnOOH phase, but not the zinc manganate products described in other reports. Further, elemental mapping using 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 $\text{ZnSO}_4[\text{Zn(OH)}_2]_3$ using NMR and XRD. Based on these findings, the authors postulated that during discharge, H^+ from the electrolyte converts α - MnO_2 to MnOOH , whereas OH^- from the electrolyte reacts with ZnSO_4 to form $\text{ZnSO}_4[\text{Zn(OH)}_2]_3$.

A similar conversion-type mechanism was also proposed by Lee et al.^[70] As no shifts in the XRD peak positions were detected between before and after discharge in their α -MnO₂ nanorod material, the authors speculated that charge storage did not occur via crystallographic Zn²⁺ 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 Zn₄(OH)₆SO₄·5H₂O precipitated at the end of electrochemical discharge, which formed mainly only the surface of the α -MnO₂ nanorods. As this emergent Zn₄(OH)₆SO₄·5H₂O phase is widely known to precipitate at high pH values,^[77] they tracked pH evolutions in operando, and discovered that the electrolyte pH rose during discharge and dropped during charge, consistent with onsets for Zn₄(OH)₆SO₄·5H₂O dissolution/precipitation (Figure 4b). Subsequently, Lee et al. ascribed these pH changes to originate from Mn²⁺ released into the electrolyte as an intrinsic part of the half-cell reaction occurring at the cathode. Essentially, their α -MnO₂/Zn battery operates on electrolyte equilibrium between two distinct divalent cations. During discharge, Mn²⁺ is released at the cathode during battery discharge, generating a high pH and subsequent Zn²⁺ precipitation out of the

electrolyte. During charge, Mn²⁺ from the electrolyte moves back to the cathode, generating a low electrolyte pH and causing Zn₄(OH)₆SO₄·5H₂O to dissolve and release the stored Zn²⁺.

λ -MnO₂: λ -MnO₂ 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 Mg²⁺.^[40,78] λ -MnO₂ (or spinel Mn₂O₄) crystals exhibit a cubic phase when all the lattice Mn atoms are in the +4 oxidation state. However, the partial reduction of Mn⁴⁺ to Mn³⁺ during stepwise discharge results in Jahn–Teller distortions which elongate the MnO₆ octahedra along the *c*-axis, thus triggering a cubic-to-tetragonal conversion in unit cell symmetry.^[79]

For cubic λ -MnO₂, Nolis et al. attempted to electrochemically insert Zn²⁺ into the host lattice, but ex situ XRD patterns suggested that the main constituent of the discharged electrode was the parent cubic λ -MnO₂ phase itself. Additionally, new minor phases including ZnO and Zn₂Mn₃O₈ were also observed. Further using 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 Zn²⁺ into cubic λ -MnO₂.

Figure 4. A Zn/ α -MnO₂ battery cyclized in 1 M ZnSO₄. a) TEM image of a discharged α -MnO₂ 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.^[70] Copyright 2016, John Wiley and Sons. c) Schematic of the Zn²⁺ migration path in spinel ZnMn₂O₄ (gray sphere: Zn, red sphere: O, purple octahedra: MnO₆). d) The 1st and 2nd charge–discharge cycles for β -MnO₂ at 0.32 C in 3 M Zn(CF₃SO₃)₂. e) XRD data collected at various stages A to J as indicated in (d). Reproduced with permission.^[39] Copyright 2017, Springer Nature.

For tetragonal λ - MnO_2 , the lattice Zn^{2+} mobility has been probed by simulations. High diffusion barriers for Zn^{2+} migration have been predicted.^[80] Here, it is useful to note that Zn^{2+} occupies 8a-sites in tetragonal ZnMn_2O_4 spinel, and in order to move to a neighboring 8a-site, 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 Zn^{2+} migration.

To verify this claim experimentally, Knight et al. attempted extracting Zn^{2+} from tetragonal ZnMn_2O_4 through chemical methods.^[81] They used two different oxidizing agents to chemically extract zinc, 1) NO_2BF_4 in acetonitrile medium and 2) H_2SO_4 aqueous solution. One key difference in results between applying these two methods is that unlike the treatment with NO_2BF_4 , the treatment of spinel ZnMn_2O_4 with H_2SO_4 aqueous solution can result in dissolution of Mn ions from the spinel ZnMn_2O_4 . This difference leads to a disparity in the amount of Zn^{2+} ions extracted from the spinel framework. While only a negligible amount of Zn^{2+} ions could leach out on the treatment of ZnMn_2O_4 with NO_2BF_4 , an appreciable amount of Zn^{2+} ions could leach out on treatment of ZnMn_2O_4 with a H_2SO_4 aqueous solution.

They proposed that, because sulfuric acid treatment partially dissolves Mn atoms from the spinel framework (unlike NO_2BF_4 treatment), a Mn-deficient spinel structure is obtained. Creation of vacant 16d-sites reduces the electrostatic repulsion between Mn ions and Zn^{2+} as 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 $\text{ZnMn}_{1.86\ 0.14}\text{O}_4/\text{C}$ for ZIAB cathodes, which could deliver a high capacity retention of 94% after 500 cycles at a high current rate of $500\ \text{mA g}^{-1}$.^[82]

Other Polymorphs: γ , δ , β polymorphs of MnO_2 have also been studied for ZIAB cathode applications.^[36,38,43,44]

For γ - MnO_2 , the crystal structure exhibits two types of tunnels, 1×1 and 1×2 (see Section 2.1 and Figure 2c). Using XAS, Alfariqi et al. showed that electrochemical Zn^{2+} insertion in γ - MnO_2 induces phase segregation in γ - 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 (Zn^{2+} insertion), the HCP-type oxygen sublattice in 1×1 tunnels of γ - MnO_2 shears to a CCP-type sublattice, transforming the material to a spinel ZnMn_2O_4 (with Mn^{3+}). With further discharge, the 1×2 tunnels of γ - MnO_2 expand slightly and form tunnel-type $\gamma\text{Zn}_x\text{MnO}_2$ (with Mn^{2+}). At the final discharge stages, tunnels of $\gamma\text{Zn}_x\text{MnO}_2$ formed expand further, transforming it to a layered-type Zn_xMnO_2 .

For δ - MnO_2 , exactly what discharge product forms due to the electrochemical interaction of Zn^{2+} with δ - MnO_2 remains ambiguous.^[38,44] Alfariqi et al. initially claimed that Zn^{2+} insertion causes the δ - MnO_2 structure to transform to a mixture of ZnMn_2O_4 spinel and Zn-birnessite,^[38] but they later amended the exact reaction mechanism to be: δ - $\text{MnO}_2 \rightarrow \text{Zn}$ -inserted δ - $\text{MnO}_2 \rightarrow \text{Zn}$ -buserite $\rightarrow \text{ZnMn}_2\text{O}_4$ spinel, based on in situ XRD, ex situ XRD, and XAS data.^[44]

For β - MnO_2 , Islam et al. showed that Zn^{2+} insertion results in the formation of many phases: Zn-buserite, Zn-birnessite, and spinel ZnMn_2O_4 in the bulk material, and

$\text{ZnSO}_4 \cdot 3\text{Zn}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ precipitation on the electrode surface.^[36] However, XRD results showed that over prolonged charge–discharge cycles, spinel ZnMn_2O_4 was the predominant bulk phase.

On the other hand, Zhang et al. proposed an alternate Zn^{2+} insertion mechanism in β - MnO_2 .^[39] Through XRD analysis, they pointed out that β - MnO_2 transformed to Zn-buserite at the end of the first discharge step (Figure 4d,e), and ascribed it to Zn^{2+} and water coinsertion along with manganese dissolution. Thereafter, the subsequent charge–discharge cycling steps showed a reversible intercalation/deintercalation of Zn^{2+} in the water-containing buserite framework with a high capacity of $\approx 150\ \text{mAh g}^{-1}$ and reversible up to 2000 cycles.

2.1.2. Factors Contributing to Capacity Fading in MnO_2 Polymorphs

The charge–discharge cycling stability for most of the reports on 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 MnO_2 electrodes: 1) irreversible phase transformation to spinel ZnMn_2O_4 phase, and 2) loss of redox-active Mn ions from the electrode.

Prolonged cycling of MnO_2 polymorphs including β , γ , and δ polymorphs has been shown to generally result in irreversible phase transformations, leading to the emergence of spinel ZnMn_2O_4 as the dominant phase.^[36,38,43,44] The spinel ZnMn_2O_4 has a very high negative formation energy ($-1293.3\ \text{kJ mol}^{-1}$),^[83] making the compound very stable and Zn extraction during the charging step highly unfavorable. The spinel ZnMn_2O_4 also has very high migration barriers which make lattice mobility of 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 λ - MnO_2 , partial vacancies on the Mn sublattice can reduce Zn^{2+} – $\text{Mn}^{3+/4+}$ electrostatic repulsion during Zn-ion lattice migration and help improve the reversibility of the spinel- ZnMn_2O_4 crystal structure.^[82] Additionally, the Zn^{2+} diffusion coefficient in Mn-deficient spinel ($0.4 \times 10^{-11}\ \text{cm}^2\ \text{s}^{-1}$, using galvanostatic intermittent titration technique) was found to be comparable to the Li^+ diffusion coefficient in spinel framework ($\approx 10^{-10}\ \text{cm}^2\ \text{s}^{-1}$).^[84]

Another reason attributed to the capacity fading is the loss of redox-active Mn atoms from MnO_2 electrodes via Mn^{2+} dissolution,^[43,46,85,86] as discussed in Section 4.1.2. Pan et al. demonstrated that adding Mn^{2+} in the electrolyte can alleviate this issue.^[42] The extra dissolved Mn^{2+} in the electrolyte shifts the $\text{MnO}_{2(s)}/\text{Mn}^{2+}_{(aq)}$ 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 Mn^{2+} in the electrolyte in mitigating the capacity fade.^[39] Using the Nernst equation, the thermodynamic potentials for precipitating MnO_2 (Mn^{4+}) and Mn_2O_3 (Mn^{3+}) from $0.1\ \text{M}\ \text{Mn}(\text{CF}_3\text{SO}_3)_2$ in $3\ \text{M}\ \text{Zn}(\text{CF}_3\text{SO}_3)_2$ 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_x nanosheets on cathode surface (Figure 5b), when the cathodes were charged above the mentioned voltages. These

Table 1. Electrochemical performance for various manganese oxides ZIAB cathodes. Unless otherwise stated, the anode is zinc metal.

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.
α -MnO ₂	1 M ZnSO ₄	Stainless steel	XPS, ex situ XRD	6 C	1.5	≈210	≈100% at 100	[45]
α -MnO ₂ /CNT	2 M ZnSO ₄ + 0.5 M MnSO ₄	Stainless steel	XPS, ex situ XRD	5 A g ⁻¹	≈1.4	400	≈100% at 500	[46]
α -MnO ₂	1 M ZnSO ₄	Stainless steel	Ex situ XRD, XAS, TEM, atomic absorption spectroscopy	≈10 mA g ⁻¹	≈1.5	205	62% at 30	[48]
α -MnO ₂	2 M ZnSO ₄ + 0.1 M MnSO ₄	Carbon sheet	STEM-HAADF, TEM, NMR	5 C	1.44	285	92% at 5000	[42]
α -MnO ₂	1 M ZnSO ₄	Stainless steel	—	83 mA g ⁻¹	≈1.4	≈200	≈54% at 75	[37]
β -MnO ₂	1 M ZnSO ₄	a)	XAS, in situ XRD, XPS	200 mA g ⁻¹	≈1.4	≈180	75% at 200	[36]
β -MnO ₂	3 M Zn(CF ₃ SO ₃) ₂ + 0.1 M Zn(CF ₃ SO ₃) ₂	Titanium	TEM-EDS, XPS, XAS	6.5 C	≈1.4	≈150	94% at 2000	[39]
γ -MnO ₂	1 M ZnSO ₄	Stainless steel	XAS, TEM, in situ XRD	50 mA cm ⁻²	1.5	≈200	63% at 40	[43]
δ -MnO ₂	1 M ZnSO ₄	Stainless steel	Ex situ XRD	83 mA g ⁻¹	≈1.5	≈170	≈91.8% at 100	[38]
δ -MnO ₂	1 M ZnSO ₄	Stainless steel	In situ XRD, XAS	100 mA g ⁻¹	≈1.3	≈225	≈43% at 50	[44]
λ -MnO ₂	1 M ZnSO ₄	Carbon fiber cloth	XPS	—	≈1.5	—	—	[40]
λ -MnO ₂ (Pt anode)	1 M Zn(NO ₃) ₂	Stainless steel	TEM-EDS, XAS, ex situ XRD	—	—	—	—	[197]
ZnMn _{1.86} 0.14O ₄ /C	3 M Zn(CF ₃ SO ₃) ₂	Titanium	Raman, sXAS, ex situ XRD	50 mA g ⁻¹	≈1.4	150	94% at 500	[82]
spinel Mn ₃ O ₄	2 M ZnSO ₄	Stainless steel	Ex situ XRD, HRTEM, SEM-EDS	500 mA g ⁻¹	≈1.4	≈140	≈72% at 300	[41]
α -Mn ₂ O ₃	2 M ZnSO ₄ + 0.1 M MnSO ₄	Stainless steel	Ex situ XRD, HRTEM, EDS	2 A g ⁻¹	≈1.4	≈75	≈66% at 2000	[68]
V _{0.05} MnO ₂	1 M ZnSO ₄	Stainless steel	Ex situ XRD	66 mA g ⁻¹	≈1.2	266	≈49% at 100	[33]
Electrolytic manganese dioxide (EMD MnO ₂)	2 M ZnSO ₄ + 0.1 M MnSO ₄	Carbon paper	In situ XRD, EELS, SEM-EDS	60 mA g ⁻¹	≈1.35	≈220	≈100% at 100	[198]
Akhtenskite or EMD MnO ₂	2 M ZnSO ₄ + 0.2 M MnSO ₄	Carbon fiber paper	Ex situ XRD	6.5 C	≈1.4	≈50	≈100% at 10 000	[47]

a) No current collector was used, instead a self-standing electrode with carboxymethyl cellulose and styrene-butadiene rubber was used.

nanosheets kept the electrode intact, prevented electrode rupture, and hence mitigated the capacity fading, unlike the case where Mn²⁺ was not preadded in the electrolyte (Figure 5c).

2.1.3. Summary

To summarize, MnO₂ polymorphs especially the α and β polymorphs have shown high capacities with good capacity retentions (Table 1), making them good candidates for BESS. However, the Zn²⁺ storage mechanism for MnO₂ polymorphs is still ambiguous. K⁺, Na⁺, Mg²⁺, and H₂O from synthesis precursors can intercalate into the MnO₂ crystals tunnel/layers and change the valence state of Mn in MnO₂, making a one-to-one comparison between each study harder.^[87,88]

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 Zn²⁺ insertion in aqueous electrolyte. We speculate three important steps are responsible for this phase transformation: 1) ingress of water molecules, 2) vacancy creation via Mn²⁺ dissolution, and 3) Zn²⁺ insertion. Phase transformation to structures with high interlayer spacing (7 Å for birnessite^[91] and 11 Å for buserite^[92,93]) also indicate that Zn²⁺ might be entering the crystal

with attached water molecules.^[69] Therefore, the role of water for Zn²⁺ insertion in the MnO₂ 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, xero-V₂O₅, has been of immense interest for ZIABs, considering its good performance with other multivalent ions such as Mg²⁺ in the water-based electrolyte.^[95,96] Additionally, metal vanadates and vanadium-based NASICON have also been investigated for ZIABs.^[23,26]

2.2.1. Bilayered Vanadium Pentoxide

Xero-V₂O₅ exhibits distorted VO₆ polyhedra and forms a bilayered structure.^[94] These bilayers expand when water molecules insert between them (Figure 6a) to form V₂O₅·nH₂O.^[97] The H₂O interlayer between the V₂O₅ bilayers apparently plays a crucial role in facilitating cation insertion into the xero-V₂O₅ host lattice and enhancing electrode cyclability, in particular via an electrostatic shielding mechanism. The interlayer H₂O reduces

Figure 5. a) An α - MnO_2 cathode material cycled against a Zn metal anode, using an electrolyte of 2 M ZnSO_4 with or without 0.1 M MnSO_4 additive. Reproduced with permission.^[42] Copyright 2016, Springer Nature. SEM images and elemental maps of a β - MnO_2 cathode after 10 charge/discharge cycles in 3 M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ b) with 0.1 M $\text{Mn}(\text{CF}_3\text{SO}_3)_3$ additive and c) without 0.1 M $\text{Mn}(\text{CF}_3\text{SO}_3)_3$ additive. Reproduced with permission.^[39] Copyright 2017, Springer Nature.

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- V_2O_5 /reduced graphene oxide ($\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ /RGO) system. They noticed deteriorated cycling performance when the crystal water in the $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ /RGO cathode was eliminated by heating (Figure 6b).^[59] This observation indicated that water plays a crucial role in Zn^{2+} insertion, similar to an observation made in the case of Mg^{2+} .^[99]

An analogous material, $\text{Zn}_{0.25}\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ was studied as a cathode in a ZIAB by Kundu et al.^[51] The crystal structure of

$\text{Zn}_{0.25}\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ is very similar to $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$, with one key difference being that the material has also ZnO_6 octahedra along with H_2O molecules in between the V_2O_5 bilayers. Electrochemical Zn^{2+} insertion/deinsertion in 1 M ZnSO_4 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 Zn^{2+} insertion at the interface.^[100–102]

Nonetheless, from a crystallographic perspective, there are conflicting reports on the physical effect of water on the V_2O_5

Figure 6. a) The $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ crystal structure (blue spheres: O atoms in water molecules). b) The respective rate-capabilities of cathode materials made of $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ /reduced graphene oxide (VOG) composite or a VOG composite preannealed at 350 °C (VOG-350), cycled against a Zn-metal anode in 3 M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ electrolyte. Reproduced with permission.^[59] Copyright 2017, John Wiley and Sons. c) Schematic showing the crystal structure transformations for $\text{Zn}_{0.25}\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ with Zn insertion/extraction processes during electrochemical cycling, according to Kundu et al. (gray spheres: Zn^{2+} , gray octahedra: ZnO_6 , red polyhedra: $\text{VO}_6/\text{VO}_5/\text{VO}_4$, red spheres: O, blue spheres: H). Reproduced with permission.^[51] Copyright 2016, Springer Nature.

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 V_2O_5 bilayers during Zn^{2+} insertion, and inferred that Zn^{2+} insertion causes lattice H_2O molecules to be expelled out of V_2O_5 bilayers (Figure 6c), bringing the V_2O_5 bilayers closer due to increased electrostatic attractions.

However, other studies demonstrated a lattice expansion instead along the axis orthogonal to the V_2O_5 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 Zn^{2+} along with few water molecules from the electrolyte solvent. Similar observations have also been made during Mg^{2+} 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 VO_4^{3-} (orthovanadates), $V_2O_7^{4-}$ (pyrovanadates), or $[V_3O_8]^{n-}$ 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 $M_xV_yO_z$ (M = metal cation) crystallizing in either a layered- or a tunnel-type structure. In the case of a layered framework, for instance, in LiV_3O_8 , the layers consist of negatively charged $[V_3O_8]^-$ 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 LiV_3O_8 , $H_2V_3O_8$, $Na_{0.33}V_2O_5$, $\alpha-Zn_2V_2O_7$, $Fe_5V_{15}O_{39}(OH)_9 \cdot 9H_2O$, $Na_2V_6O_{16} \cdot 3H_2O$, $Ca_{0.25}V_2O_5 \cdot nH_2O$ have been investigated so far.^[49,50,52–55,58] However, the Zn^{2+} insertion mechanism is not unique and may differ for each material. We discuss examples here in this section: LiV_3O_8 and $Na_{0.33}V_2O_5$.

LiV_3O_8 (LVO) is comprised of layers of VO_5 trigonal pyramids and VO_6 octahedra, and lithium as the interlayer bridging atoms.^[105] Alfaruqi et al. studied the Zn^{2+} -insertion mechanism in LVO in detail using synchrotron XRD.^[50] The initial Zn^{2+} -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 $ZnLiV_3O_8$ that segregates out. The final stage involves Zn^{2+} insertion via solid-solution behavior in a $Zn_xLiV_3O_8$ phase ($x > 1$).

On the other hand, $Na_{0.33}V_2O_5$ (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 Zn^{2+} insertion was observed. Instead, a new phase $Zn_xNa_{0.33}V_2O_5$ ($0 < x < 0.96$) emerged alongside the pristine $Na_{0.33}V_2O_5$ as the discharging proceeded.

Figure 7. a) Crystal structure of hexagonal NASICON $NaV_2(PO_4)_3$ (orange polyhedra: VO_6 , magenta polyhedra: PO_4 , 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.

2.2.3. Vanadium-Based Polyanionic Structures

The vanadium-based NASICON framework (Figure 7a) consists of VO_6 octahedra and PO_4 tetrahedra having a general formula of $A_xV_2(PO_4)_3$ where A can be a monovalent/divalent cation. Owing to an inductive effect exerted by phosphate

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 $\text{NaV}_2(\text{PO}_4)_3$ was used as a ZIAB cathode.^[61] While the previously discussed xero- V_2O_5 and metal vanadates exhibited an average intercalation voltage of ≈ 0.7 V (vs Zn^{2+}/Zn), Zn^{2+} inserted at a voltage of ≈ 1.1 V (vs Zn^{2+}/Zn) in $\text{NaV}_2(\text{PO}_4)_3$.

A fluorophosphate structure such as $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ can push the intercalation voltage even higher when compared to $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ 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 to MnO_2 polymorphs. Water plays a pivotal role in delivering these high capacities and high reversibility, however, the mechanism is still disputed.

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).^[39] 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]

2.3. Prussian Blue Analogs

The Prussian blue material is a metal–organic framework (Figure 7b) with a chemical formula of $\text{A}_x\text{MM}'(\text{CN})_6 \cdot y\text{H}_2\text{O}$, 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 $\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ (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.^[36,51] Zhang et al. synthesized $\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ with different crystallographic facets (Figure 7c–e) and observed a different electrochemical cycling behavior for each morphology.^[64] As shown

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 [mAh g^{-1}]	Retention (% at cycles)	Ref.
$\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}/\text{RGO}$ ($n > 1$)	3 M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$	Titanium	MAS NMR, ex situ XRD	6 A g^{-1}	≈ 0.5	≈ 230	91.3% at 900	[59]
$\text{Zn}_{0.25}\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$	1 M ZnSO_4	a)	XPS, in situ XRD	15 C	≈ 0.7	≈ 230	$\approx 91.3\%$ at 1000	[51]
Anhydrous V_2O_5	3 M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$	Titanium	TEM-EDS, XPS, ex situ XRD	5 A g^{-1}	≈ 0.6	470	91% at 4000	[57]
$\text{H}_2\text{V}_3\text{O}_8$	3 M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$	Titanium	Ex situ XRD, XPS, TEM-EDS	5 A g^{-1}	≈ 0.6	≈ 170	80% at 1000	[53]
$\text{Na}_{0.33}\text{V}_2\text{O}_5$	3 M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$	Titanium	Ex situ XRD, HRTEM	1 A g^{-1}	≈ 0.6	≈ 300	72% at 1000	[58]
$\text{Na}_2\text{V}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}$	1 M ZnSO_4	Stainless steel	XPS, in situ XRD	40 C	≈ 0.7	≈ 150	80% at 1000	[54]
$\alpha\text{-Zn}_2\text{V}_2\text{O}_7$	1 M ZnSO_4	Stainless steel	Ex situ XRD	4 A g^{-1}	≈ 0.7	≈ 138	85% at 1000	[49]
$\text{Fe}_5\text{V}_{15}\text{O}_{39}(\text{OH})_9 \cdot 9\text{H}_2\text{O}$	0.3 M $\text{Zn}(\text{TFSI})_2$	Titanium	In situ XRD, XPS	5 A g^{-1}	≈ 0.6	125	80% at 300	[55]
$\text{Ca}_{0.25}\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$	1 M ZnSO_4	a)	XPS, ex situ XRD	80 C	≈ 0.7	≈ 70	96% at 3000	[52]
VO_2	3 M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$	Titanium	In situ XRD, HRTEM, XPS	300 C	≈ 0.6	171	–	[112]
VO_2	3 M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$	Carbon paper	Raman, XPS, ex situ XRD	10 mA g^{-1}	≈ 0.7	274	79% at 10 000	[113]
$\text{Na}_3\text{V}_2(\text{PO}_4)_3$	0.5 M $\text{Zn}(\text{CH}_3\text{COO})_2$	Nickel foam	Ex situ XRD, HAADF-STEM	50 mA g^{-1}	1.1	97	74% at 100	[61]
$\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$	2 M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$	Titanium	XPS, ex situ XRD	1 A g^{-1}	1.62	50	94% at 4000	[60]

a) No current collector was used, instead a self-standing electrode with carboxymethyl cellulose and styrene–butadiene rubber was used.

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.
$\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$	1 M ZnSO_4	Stainless steel	–	300 mA g^{-1}	1.7	52.5	≈81% at 100	[63]
$\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$	3 M ZnSO_4	Stainless steel	Ex situ XRD	300 mA g^{-1}	1.73	59.2	80% at 200	[64]
CuFeCN_6	0.2 M ZnSO_4	Carbon cloth	–	60 mA g^{-1}	1.73	52.5	96.3% at 100	[65]

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)

A $\text{Mo}_{2.48}\text{VO}_{9.93}$ compound built from MO_6 octahedra ($\text{M} = \text{V}, \text{Mo}$) 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_6S_8 is one of these compounds which contains multiple cation insertion sites (Figure 8b). Mo_6S_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.

Table 4. Electrochemical performance for other inorganic and organic materials 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	[199]
Mo_6S_8	1 M ZnSO_4	Carbon	Ex situ XRD	600 mA g^{-1}	≈0.35	85	90% at 350	[119]
$\text{Mo}_{2.48}\text{VO}_{9.93}$	0.5 M $\text{Zn}(\text{CH}_3\text{COO})_2$	Carbon strip	HRTEM, STEM-EDS	10 mA g^{-1}	≈0.4	220	≈70% at 30	[118]
$\text{V}_{0.95}\text{Al}_{0.05}\text{O}_{1.52}(\text{OH})_{0.77}$	1 M ZnSO_4	Stainless steel	Ex situ XRD, XANES	15 mA g^{-1}	≈0.6	105	≈60% at 50	[168]
Calix(4)quinone	3 M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$	Titanium	In situ Raman, in situ FTIR	500 mA g^{-1}	1 V	335	87% at 1000	[120]
Tetrachloro-1,4-benzoquinone	1 M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$	Graphite foil	In situ XRD, SEM-EDX	≈43 mA g^{-1}	1.1	200	≈65% at 30	[200]
Poly(benzoquinonyl sulfide)	3 M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$	Stainless steel	Ex situ FTIR	0.2 C	0.95 V	203	86% at 50	[201]

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 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

Figure 8. a) The $\text{Mo}_{2.48}\text{VO}_{9.93}$ crystal structure viewed along the c-axis (the polyhedra colors are indicated as follows, green: $\text{Mo}^{5+}/\text{V}^{4+}$, red: $\text{Mo}^{6+}/\text{V}^{5+}$, blue: $\text{Mo}^{6+}/\text{Mo}^{5+}$, orange: Mo^{5+} , purple: Mo^{6+}). Reproduced with permission.^[195] Copyright 2013, ACS. b) The Chevrel Mo_6S_8 crystal structure showing multiple cavities where a cation can insert. Reproduced with permission.^[155] c) The Zn^{2+} insertion/deinsertion mechanism in calix(4)quinone proposed by Zhao et al. Reproduced under the terms of CC BY-NC.^[120] Copyright 2018, Science Advances (American Association for the Advancement of Science).

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 (AlCl_3) 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 (TiO_2)

TiO_2 exists in eight different types of crystal structures, with rutile, brookite, and anatase as the common polymorphs.^[122] The anatase TiO_2 crystal structure is composed of stacked TiO_6 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 TiO_2 nanotubes,^[123]

which were prepared by anodizing titanium foil (Figure 9b). Their explanation for the newfound electrochemical activity in nanotube TiO_2 as opposed to bulk TiO_2 was that by virtue of their form factor, nanotubes created shorter ion diffusion paths and a better electrolyte–electrode contact compared to bulk TiO_2 during electrochemical testing timescales. Using XPS and NMR, Liu et al. showed an electrochemical reduction of lattice titanium (Ti^{4+} to $\text{Ti}^{3+}/\text{Ti}^{2+}$) and suggested the material to be charge-compensated by lattice insertion of Al ions. Further, CV experiments of TiO_2 in chloride salts of Al, Mg, and Li showed significantly higher CV peak intensities for the AlCl_3 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 Al^{3+} , as compared to Li^+ and Mg^{2+} (53.5 pm for Al^{3+} and 76 and 72 pm for Li^+ and Mg^{2+} , respectively), resulted in facile electrochemical Al^{3+} 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 Al^{3+} (4.75 Å for Al^{3+} , 4.30 Å for Zn^{2+} , and 3.82 Å for Li^+) would most likely make its insertion into TiO_2 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, Al^{3+} has a hard charge density, implying that Al^{3+} would face more resistance during the insertion process, as compared to any other mono-/bivalent molecule of comparable size. Nonetheless,

Table 5. Electrochemical performance for various materials as AlAB electrode.

Working Electrode	Composite used – percentage	Electrolyte	Current collector	Proof of Al ³⁺ insertion	Current rate	Average voltage [V] (vs SHE)	Capacity [mAh g ⁻¹]	Retention (% at cycles)	Ref.
TiO ₂ nanotube array	TiO ₂ nanotube array – 100	1 M AlCl ₃	Epoxy resin-coated Ti foil	XPS, NMR	4 mA cm ⁻²	–0.81	75	>100% at 13	[123]
TiO ₂ nanoleaves	TiO ₂ :PVDF:AB – 80:10:10	1 M Al(NO ₃) ₃	Pt	XPS, XRD, NMR	0.05 A g ⁻¹	–0.82	278.1	91.6% at 300	[126]
TiO ₂ nanospheres	TiO ₂ :PVDF:AB – 80:10:10	1 M AlCl ₃	Ni	–	0.15 C	–0.84	183	96.67% at 25	[130]
TiO ₂ /CNT nanocomposite	TiO ₂ :PVDF:AB – 80:10:10	1 M AlCl ₃	Ni	–	1 C	–0.85	170	94.12% at 100	[131]
TiO ₂ nanotube array	TiO ₂ nanotube array – 100	Different concentrations of Al ₂ (SO ₄) ₃ , AlCl ₃ with NaCl as additive	Epoxy resin-coated Ti foil	XPS	4 mA cm ⁻²	–0.77	74.8	–	[135]
TiO ₂ nanotube array	TiO ₂ nanotube array – 100	Al ₂ (SO ₄) ₃ and AlCl ₃ at different pH	Epoxy resin-coated Ti foil	XPS	–	–	–	–	[136]
G-TiO ₂	G-TiO ₂ :PVDF – 80:20	0.25 M AlCl ₃	Stainless steel	XRD	6.25 A g ⁻¹	–0.73	50 mAh g ⁻¹	64% at 125	[132]
G-TiO ₂	G-TiO ₂ :PVDF – 80:20	0.5 M AlCl ₃	Stainless steel	XRD	6.25 A g ⁻¹	–0.73	40 mAh g ⁻¹	>100% at 90	[133]
CuFe–PBA	CuFe–PBA:CNT:PTFE – 80:16:8	1 M Al(NO ₃) ₃	Ti rods	XRD, TEM-EDS	1 C	0.72	55	–	[137]
Al _{0.2} CuFe–PBA	Al _{0.2} CuFe–PBA:CNT:PTFE – 80:16:8	1 M Al(NO ₃) ₃	AC	–	5 C	0.5	30	83.3% at 1000	[137]
CuHCF	CuHCF:AB:PTFE – 80:15:5	0.5 M Al ₂ (SO ₄) ₃	Ti mesh	–	400 mA g ⁻¹	0.66, 0.83	40	54.9% at 1000	[138]
CuHCF	CuHCF:SuperP:PVDF – 80:10:10	Nitric acid + 1 M Al(NO ₃) ₃	Carbon cloth	–	5 C	0.76	49	–	[116]
CuHCF	Cu-HCF:carbon black (CB):Nafion – 80:10:10	1 mol dm ⁻³ AlCl ₃ and 1 mol dm ⁻³ KCl	Sigracell PV10	–	20 C	1.5 (full cell)	10 mAh g ⁻¹	90% at 1814	[202]
Xero-V ₂ O ₅	Xero-V ₂ O ₅ :PTFE:carbon black	1 M AlCl ₃	Carbon paper	XPS, XRD	60 mA g ⁻¹	0.48	120	62.5% at 13	[139]
Exfoliated graphite	Graphite:AB:PTFE – 80:10:10	Al ₂ (SO ₄) ₃ /Zn(CH ₃ COO) ₂	Carbon rod	HRTEM, SAED, XRD	0.5 A g ⁻¹	0.24	80 mAh g ⁻¹	94% at 200	[141]
Na ₃ V ₂ (PO ₄) ₃	NVP:CB:PVDF – 80:10:10	0.1 M AlCl ₃	–	Electron probe micro analysis (EPMA), NMR, XRD, XPS	60 mA g ⁻¹	0.62	100	40% at 40	[145]
PPy-coated MoO ₃ nanotubes	MoO ₃ :AB:PTFE – 80:10:10	0.5 M Al ₂ (SO ₄) ₃	Carbon rod	EDS, XRD, XPS	2 A g ⁻¹	–	30 W h kg ⁻¹	93% at 1800	[146]
2D Ti ₃ C ₂ T _x	Ti ₃ C ₂ T _x :OLC:PTFE – 85:10:5	1 M Al(NO ₃) ₃ , Al ₂ (SO ₄) ₃	Freestanding	–	–	–	–	–	[147]

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 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 H₂O to the strong solvation interactions between Al ions and H₂O. Additionally, an increased H₂ overpotential can result from varying bonding strengths of hydrogen species on different electrode surfaces, as observed for various metal surfaces.^[127,128] Thus,

Figure 9. a) The crystal structure of anatase TiO₂ (blue spheres: Ti, red spheres: O). b) SEM image of as-prepared anatase TiO₂ nanotube arrays, and c) cyclic voltammograms (CVs) of the as-prepared anatase TiO₂ nanotube arrays in 1 M AlCl₃, MgCl₂, and LiCl aqueous electrolytes, scanned at 20 mV s⁻¹. Reproduced with permission.^[123] Copyright 2012, RSC. d) Low magnification TEM image of the as-prepared black-anatase TiO₂ nanoleaves (inset: photograph of willow leaves for morphology comparison). e) The first discharge profiles of black-anatase TiO₂ nanoleaves and commercial white-anatase TiO₂ electrodes at a current rate of 0.05 A g⁻¹ in 1 M Al(NO₃)₃ electrolyte, and f) the corresponding cyclic voltammograms at 1 mV s⁻¹. Reproduced with permission.^[126] Copyright 2013, RSC.

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 TiO₂.

By modifying anatase TiO₂ 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(NO₃)₃ aqueous solution.^[126] Mesoporous TiO₂ 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 TiO₂ (Figure 9e) showed similar behavior as proposed for Li-ion storage in TiO₂.^[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 TiO₂. 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 Al³⁺ concentrations with Ti reduction (Ti⁴⁺ to Ti³⁺) 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 TiO₂ lattice. He et al. claimed that the amount of oxygen vacancies in TiO₂ nanoleaves was more than what was present in commercial TiO₂, 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 Ti³⁺ to Ti²⁺ during Al³⁺ insertion. Of note, the reduced gaps between the peak-onset voltages of the cathodic and anodic sweeps for these TiO₂ nanoleaves (Figure 9f) indicated that Al³⁺ insertion/extraction occurred more readily in anatase TiO₂ 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 TiO₂ nanoleaves to nanoparticle ordering within the nanoleaves which aided lattice intercalation, increased surface areas at the electrode–electrolyte interfaces, and the structural robustness of TiO₂.

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 TiO_2 nanospheres and testing it in 1 M AlCl_3 for Al insertion.^[130] 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 TiO_2 /carbon nanotube (CNT) nanocomposite anode material,^[131] 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 TiO_2 nanospheres in their previous work.^[130] Kazazi et al. attributed this improved performance to the enhanced surface area and conductivity network around TiO_2 due to CNT incorporation.

Exploring the same concept of performance enhancement due to better electrical conductivity, Lahan et al. tested

Al insertion in anatase TiO_2 with different conductive additives (graphene, CNT, and Ag).^[132] Graphene- TiO_2 composites showed clear anodic and cathodic peaks in 1 M AlCl_3 , whereas pure TiO_2 without any conductive additives did not (Figure 10a,b). Increasing electrochemical activity was observed in the following order: graphene- TiO_2 > CNT- TiO_2 > Ag- TiO_2 > TiO_2 . 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 Al^{3+} -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

Figure 10. The respective CVs for a) a graphene- TiO_2 composite and b) TiO_2 , in 1 M AlCl_3 electrolyte at a scan rate of 5 mV s^{-1} . Reproduced with permission.^[132] Copyright 2017, ACS. c) Ex situ XRD patterns of graphene- TiO_2 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 AlCl_3 electrolyte (XRD peaks for anatase TiO_2 is denoted as "A"). Reproduced with permission.^[133] Copyright 2018, Springer-Verlag GmbH Germany. d) Typical CV curves of the as-prepared anatase TiO_2 nanotube arrays at 10 mV s^{-1} in electrolytes of 0.25 M $\text{Al}_2(\text{SO}_4)_3$ with varying concentrations of NaCl added. Reproduced with permission.^[135] Copyright 2014, Elsevier Ltd. e) Faradic resistance (R_f) of TiO_2 electrodes as a function of polarization time in chloride-based and sulfate-based electrolytes at various pH. Reproduced with permission.^[136] 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 Al₂(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 (*R_p*) 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 *R_p* versus time curve showed an initial increase and subsequent decrease in *R_p*. 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 *R_p* 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.,^[135] 3) for a fixed anion, the *R_p* 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.^[116] 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.

Figure 11. a) The Al/Cu and Fe/Cu elemental ratios measured using TEM-EDS for CuFe-PBA after electrochemical cycling against $\text{Al}_x\text{CuFe-PBA}$ in 1 M $\text{Al}(\text{NO}_3)_3$ electrolyte, (A to F indicate electrode at various stages of charge–discharge cycle) and b) TEM-EDS elemental maps of CuFe-PBA for sample C in (a). Reproduced with permission.^[137] Copyright 2014, John Wiley and Sons. c) CVs demonstrating the reversible insertion of a variety of trivalent ions in CuHCF in 1 M concentrations of the respective nitrate-based electrolytes at pH = 2. Reproduced with permission.^[116] Copyright 2015, John Wiley and Sons. d) Ex situ XRD patterns of pristine and cycled V_2O_5 at various states of charge/discharge. The peak at 26.4° corresponds to the graphite substrate. e) Specific capacity as a function of cycle number at different current densities for Xero- V_2O_5 in 1 M AlCl_3 . Reproduced with permission.^[139] Copyright 2016, RSC.

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.^[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_2O_5)

The layered V_2O_5 structure along with a high $\text{V}^{5+}/\text{V}^{4+}$ redox potential makes it suitable as an AIAB cathode. González et al.

showed reversible intercalation of Al ions into V_2O_5 xerogels, in 1 M $AlCl_3$ aqueous electrolyte.^[139] XPS results confirmed the intercalation of Al ion and concomitant reduction of the average oxidation state of lattice vanadium in discharged V_2O_5 cathodes. The ex situ XRD results (Figure 11d) of electrodes obtained at different stages of discharging indicated progressive amorphization of V_2O_5 . González et al. also observed a significant drop in gravimetric capacity on cycling V_2O_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_2O . 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.

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.^[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,^[141] which is produced by a two-step process: first, H_2O and NO_3^- molecules are electrochemically inserted into pristine graphitic layers; second, under subsequent application of appropriate voltages, H_2O 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 $Al_2(SO_4)_3/Zn(CH_3COO)_2$ 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 $Al_2(SO_4)_3/Zn(CH_3COO)_2$ originated from Al-ion intercalation alone and that other spectator ions (Zn^{2+} , H^+ , CH_3COO^- , or SO_4^{2-}) did not cointercalate. With discharge, graphite sheets also exhibited an increase in interlayer distances by 5 Å (Figure 12c,e), whereas 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 HRTEM image and SAED pattern (Figure 12g,h) were identical to that of the pristine sample, essentially

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 $Al_2(SO_4)_3/Zn(CH_3COO)_2$. 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.^[141] Copyright 2016, ACS.

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	$\text{Na}_3\text{V}_2(\text{PO}_4)_3$	$\text{Na}_{2.8}\text{V}_2(\text{PO}_4)_{3.5}$	$a = 8.735(5)$ $c = 21.82(1)$
After first charge	$\text{Na}_{1.1}\text{V}_2(\text{PO}_4)_3$	$\text{Al}_{0.06}\text{Na}_{0.94}\text{V}_2(\text{PO}_4)_{2.6}$	$a = 8.401(1)$ $c = 21.444(4)$
After charge + discharge	$\text{Al}_{0.3}\text{Na}_{1.1}\text{V}_2(\text{PO}_4)_3$	$\text{Al}_{0.25}\text{Na}_{0.81}\text{V}_2(\text{PO}_4)_{2.2}$	$a = 8.51(1)$ $c = 21.81(3)$

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 Al³⁺, modified forms of graphene may aid as they have in the past for other materials.^[142–144]

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

NASICON-type $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (NVP) was studied by Nacimient 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, Nacimient 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, Nacimient 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 $\text{Ti}_3\text{C}_2\text{T}_x$ (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_3C_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/hydrogen coininsertion. Moreover, at the electrodes, uncontrolled dissolution of redox-active transition-metal components, and O_2 -driven parasitic reactions (from dissolved 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 pseudocapacitive effects on electrode surfaces rather than by ion intercalation into bulk crystal structures. Such behaviors have been reported by multiple studies on ZIABs,^[52,56,57,112,113] and AIABs.^[116,138] How strongly the MV-cation mobilities are limited can depend considerably on the crystal structure of the host material.

On a first-principle basis, Rong et al. simulated host materials which normally support Li-ion intercalation (spinel Mn_2O_4 , olivine FePO_4 , layered NiO_2 , and orthorhombic $\delta\text{-V}_2\text{O}_5$) for MV-ion insertion.^[148] They point out that every intercalating cation has an energetically preferred anion-coordination environment 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_2O_4 (Figure 13a) would be reduced as Zn^{2+} occupies tetrahedral sites in ZnMn_2O_4 at room temperature (the tetrahedral configuration being the most energetically stable coordination for Zn^{2+} within an oxygen sublattice). This prediction was later verified experimentally by Knight et al. through actual electrochemical measurements.^[81]

Besides the stable coordination environments of the intercalating cation within the lattice, the transitory coordination environments 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_2O_5 and spinel Mn_2O_4 crystal structures using first principles. During ion hopping, the coordination configuration changes between octahedra and square pyramids in layered V_2O_5 , whereas the coordination configuration changes in spinel Mn_2O_4 (Figure 13b) are between octahedra and tetrahedra.^[149] A change from a coordination 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 layered V_2O_5 than for spinel Mn_2O_4 (Figure 13a,c). This prediction is consistent with the high cation mobilities observed in layered V_2O_5 -based electrode materials for ZIABs and AIABs.^[57,139]

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 occupancies 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-coordination 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 drastically.^[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 $\lambda\text{-MnO}_2$). Transition-metal vacancies can be introduced into the crystal structure via two methods: 1) by modifying atmospheric conditions or solution-matrix conditions during syntheses,^[150] e.g., Sánchez and Pereira-Ramos saturated a sol-gel mixture with CO_2 ultimately producing a Mn-vacancy-rich spinel ($\text{Mn}_{2.15}\text{Co}_{0.37}\text{O}_4$) which demonstrated reversible intercalation of Mg^{2+} unlike the stoichiometric compound 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 $\gamma\text{-Fe}_2\text{O}_3$ 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 interactions with the mobile cation, 2) a bigger anionic radius which enlarges openings in the host structure for intercalation. However, using a chalcogenide framework may also reduce the intercalation potential as demonstrated in a Mo_6S_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

Figure 13. a) Migration energies calculated using first-principles simulations for various cations in spinel Mn_2O_4 . b) Migration path for cation (red sphere) between two tetrahedral sites via octahedral site in spinel Mn_2O_4 . c) Migration energies calculated for various cations in $\delta\text{-V}_2\text{O}_5$ structure. Reproduced with permission.^[148] Copyright 2015, ACS.

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*-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: MnO₂(s), Mn²⁺(aq), MnO₄⁻(aq), Mn₂O₃(s), Mn₃O₄(s), Mn(OH)₂(s), HMnO₂⁻(aq), and Mn(s) for manganese and VO₂⁺(aq), V₂O₅(s), V³⁺(aq), VOH²⁺(aq), V²⁺(aq), V₂O₃(s), V₂O₄(s), H₃V₂O₇⁻(aq), H₂VO₄⁻(aq), VO₄⁻(aq), HV₂O₅⁻(aq), and V₂O₂(s) for vanadium. During operation, when MnO₂ cathodes cycle between 0 and

1.2 V (vs SCE) at a mildly acidic pH, a thermodynamic driving force exists to reduce solid MnO₂ to aqueous Mn²⁺ according to the Pourbaix diagram. Only at applied potentials higher than 1.2 V (vs SCE) will manganese be stable as MnO₂, 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 V₂O₅, but aqueous VO²⁺.^[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 LiTi₂(PO₄)₃/LiFePO₄ aqueous lithium-ion battery in 1 M Li₂SO₄ + 0.1 M LiOH (“1” with O₂ at 6 C, “2” without O₂ at C/8, and “3” without O₂ at 6 C). d) The typical self-discharge curves of LiTi₂(PO₄)₃ in 1 M Li₂SO₄ + 0.1 M LiOH at pH 13, i) with O₂ and ii) without O₂. Reproduced with permission.^[160] Copyright 2010, Springer Nature. CVs profiles of LiFePO₄ for 50 cycles, at a scan rate of 5 mV s⁻¹ at various operating conditions in 0.5 M Li₂SO₄: e) at pH 7 without O₂; f) at pH 7 with O₂; g) at pH 7 in the solution with O₂ bubbled for 2 h. Reproduced with permission.^[161] Copyright 2010, Elsevier Ltd.

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 $Li_{3-x}Ti_2(PO_4)_3$ -cathode batteries using a hermetic Ar-purged electrolyte. By Ar-gas purging, the stability of the open-circuit potential (OCV) was extended from just 15 h in an oxygen-containing electrolyte to as much as 10 days in an oxygen-eliminated 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_2SO_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_2O (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_2O . The following reaction can occur in O_2 -free water

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 potentiodynamically 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

Because O_2 is a highly oxidizing substance, dissolved O_2 in H_2O 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.^[125,160] 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 μ_M^{int} . 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:

In presence of O_2

$$\mu_M^{\text{int}} + \frac{x}{4}\mu_{O_2}^0 + \frac{x}{2}\mu_{H_2O}^0 = \mu_{M^{x+}} + x\mu_{OH^-} \quad (7)$$

In absence of O_2

$$\mu_M^{\text{int}} + x\mu_{H_2O}^0 = \mu_{M^{x+}} + x\mu_{OH^-} + \frac{x}{2}\mu_{H_2}^0 \quad (8)$$

where $\mu_{M^{x+}}$ and μ_{OH^-} are the chemical potentials of M^{x+} and OH^- in solution, respectively, and $\mu_{O_2}^0$, $\mu_{H_2}^0$, and $\mu_{H_2O}^0$ are the chemical potentials of O_2 , H_2 , and H_2O 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

$$\mu_{M^{x+}} = \mu_{M^{x+}}^0 + \frac{kT}{xe} \ln [M^{x+}] \quad (9)$$

$$\mu_{OH^-} = \mu_{OH^-}^0 + kT \ln [OH^-] \quad (10)$$

where $\mu_{M^{x+}}^0$ and $\mu_{OH^-}^0$ 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

$$V_M = -\frac{1}{ne}(\mu_M^{\text{int}} - \mu_M^0) \quad (11)$$

where μ_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

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

In absence of O_2

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

In presence of O_2

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

In absence of O_2

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

In presence of O_2

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

In absence of O_2

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

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 $LiFePO_4$ in an increased pH of electrolyte, wherein the transition metal center reacted with OH^- .^[161] 2) Tian and Yuan measured cycling stability for the $LiMn_2O_4$ cathode in varying $LiNO_3$ 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^[37,43,44,48,50] and AIABs.^[137,138,145] Doping the transition-metal sites in the crystal structure with other elements can mitigate this issue as demonstrated previously.^[165,166] Yuan et al.^[165] showed that for aqueous lithium batteries, doping manganese in LiMn_2O_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_2O_4 spinels was improved by Al doping.^[167] For ZIABs, Jo et al. demonstrated improved structural stability and cycling performance by Al doping in Hollandite-type (isostructural to $\alpha\text{-MnO}_2$) $\text{VO}_{1.52}(\text{OH})_{0.77}$, as shown in Figure 16b.^[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_2O_3 ($-1573 \text{ kJ mol}^{-1}$) and V_2O_5 ($-1139.3 \text{ kJ mol}^{-1}$).^[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_3O^+) species along with metal cations.^[42,47,85,139] Sun et al. used electrolytic manganese dioxide (EMD– MnO_2) to demonstrate H^+ coininsertion with Zn^{2+} during discharging.^[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 $\text{ZnSO}_4 + \text{MnSO}_4$ 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_2O_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

Figure 16. a) Cyclic performance of Al-doped LiMn_2O_4 with varying Al content in 5 M LiNO_3 Reproduced with permission.^[165] Copyright 2010, Elsevier B.V. b) Charge-discharge curve for $\text{VO}_{1.52}(\text{OH})_{0.77}$ with varying Al substitution content in 1 M ZnSO_4 aqueous electrolyte. Reproduced with permission.^[168] Copyright 2017, RSC. c) Discharge curve at various cycling rates for first cycle of Zn– MnO_2 cell in 2 M ZnSO_4 . d) Discharge galvanostatic intermittent titration technique (GITT) profiles of the Zn– MnO_2 cell. Each discharge pulse was applied for 120 s at 50 mA g⁻¹ and followed by 4 h rest. e) Discharge curve for MnO_2 cathode in 0.2 M MnSO_4 solution with or without ZnSO_4 in the electrolyte. Reproduced with permission.^[47] Copyright 2017, ACS.

$\approx 130 \text{ mAh g}^{-1}$, the capacity contributions due to any proton-insertion mechanism into $\text{V}_3\text{O}_7 \cdot \text{H}_2\text{O}$ 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_3O^+ intercalation can compete with metal-cation intercalation,^[169] which might explain the dependence of capacity on increasing H_3O^+ 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 (EIs). Unfortunately, the direct decomposition products of water in an aqueous electrolyte system are either volatile gases or soluble ions.^[158] Lack of solid EIs 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_2O_4 cathodes in aqueous electrolyte ($1 \text{ M Li}_2\text{SO}_4 + 2 \text{ M ZnSO}_4$) by coating graphene layers on LiMn_2O_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

Figure 17. Schematics of the interactions a) between transition metal oxides and solvated cations in an aqueous electrolyte, illustrating water adsorption on electrode surface and water-coinsertion during cation intercalation; b) between transition metal oxides and solvated cations in a nonaqueous electrolyte, illustrating the formation of a solid electrolyte interface. Reproduced with permission.^[158] Copyright 2018, RSC. c) Uncontrolled permeation–diffusion of Li ions in uncoated LiMn_2O_4 cathodes and d) controlled permeation–diffusion of Li ions in RGO-coated LiMn_2O_4 cathodes (RGO: reduced graphene oxide). Reproduced under the terms of CC BY-NC.^[173] Copyright 2017, Science Advances (American Association for the Advancement of Science).

graphene layer when structural defects were present. Based on this, Zhi et al. proposed permeation-based mechanisms for LiMn_2O_4 cathode without and with graphene coating (Figure 17c,d). Unlike the uncoated cathode, graphene-coated cathodes showed limited diffusivity for Li^+ into LiMn_2O_4 because of limited permeation of graphene layers. Zhi et al. speculate that this leads to a suppressed Jahn–Teller distortion of LiMn_2O_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.^[178] The polymer-coated Mg and uncoated Mg were comparatively studied as anodes in full cells (anode/ V_2O_5) in 0.5 M magnesium bis(trifluoromethanesulfonyl)imide/PC+ 3 M H_2O . 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 Al 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.^[176] 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 sXAS revealed the presence of Li_2CO_3 and Li_2O which could have formed by the reduction of dissolved O_2 and CO_2 in the electrolyte.

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 LiTFSI and 7 M lithium trifluoromethane sulfonate (LiOTf)) forms a more concentrated electrolyte as compared to WIS.^[177] 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_2O_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.^[179] 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.^[174] An improved capacity and cycling stability was observed for $\text{Li}_{1.05}\text{Cr}_{0.10}\text{Mn}_{1.85}\text{O}_4$ 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.^[175] 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 formation on the electrode was studied using TEM for a $\text{LiCoO}_2\text{--Mo}_6\text{S}_8$ 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 ICP-OES analysis of cycled electrolytes. This enabled a long life of 1000 stable charge/discharge cycles for the $\text{LiCoO}_2\text{--Mo}_6\text{S}_8$ 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.^[127,128,180] 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.^[125] Alternatively, a highly concentrated electrolyte

Figure 18. a) The cycling stability and b) Coulombic efficiencies in different electrolytes for LiMn₂O₄ cathode and carbon-coated TiO₂ (or TiO₂) anode full cell at 75 mA g⁻¹ between 0.8 and 2.5 V (WIS: Water-in-salt, WIBS: Water-in-bisalt). Reproduced with permission.^[177] Copyright 2016, John Wiley and Sons. c) The highest occupied molecular orbital (HOMO) levels of TMSB, H₂O, LiTFSI, and TFSI⁻. d) Mechanism of oxidative decomposition of TMSB in a mixed electrolyte of 21 m LiTFSI–0.1 wt% TMSB, as proposed by Wang et al.^[175] TEM images of e) LiCoO₂ in 21 m LiTFSI–0.1 wt% TMSB electrolyte after 100 cycles. f) Cycled LiCoO₂ electrodes in the 21 m LiTFSI electrolyte (inset shows the amount of dissolved Co²⁺ in electrolyte measured after 50 cycles using ICP). Reproduced with permission.^[175] Copyright 2016, RSC.

can give an expanded voltage range of 3 V, as demonstrated by Suo et al.^[181] Though the effect of electrolyte pH and concentration has been discussed widely,^[10,158,182,183] the role of the current collector in H₂/O₂ 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 H₂ evolution.^[133] Lahan and Das examined how Al insertion in TiO₂ 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 TiO₂ sample coated on a graphene current collector significantly suppressed H₂ evolution and allowed for Al³⁺ 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.^[127,128] With increasing M–H bond

strength, the exchange current for H₂ 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 H₂ 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+H recombination are decreased, again reducing the exchange current density.^[127,128] To illustrate: 1) Zn falls on the left of the maximum, thus suppressing H₂ evolution to an extent and allowing the use of Zn metal as anode in ZIABs, 2) Ti falls on the extreme right of curve and shows reduced H₂ evolution as also observed by Lahan and Das; and Adams and Kundu,^[133,184] 3) Pt sits at the curve maximum and shows minimum suppression for H₂ 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 H₂-evolution potential in aqueous batteries. On the other hand, elements at the maximum of the M–H curve are suited for electrolyte studies

Figure 19. a) Exchange currents for electrolytic H₂ evolution versus metal–hydrogen bond strength for different elements. Adapted with permission.^[127] Copyright 1972, Elsevier B.V. b) Stability of specific discharge capacities of LiMn₂O₄ electrodes fabricated on different current collectors and c) the corresponding photograph of rear side of the untreated Al-foil current collector after 15 cycles (above) and chromate conversion coated (CCC) Al-foil backside after 50 cycles (below) in 2.5 M Li₂SO₄ electrolyte (pH = 7). Reproduced with permission.^[185] Copyright 2015, RSC.

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,^[132] Pt, Ti, and Ni are expected to show adequate corrosion resistance,^[159] but are expensive.^[185] As an alternative to the aforementioned current collectors, Gheyani et al. tested chromate conversion-coated aluminium foil in a 2.5 M Li₂SO₄ and showed

comparable performance to titanium foil (Figure 19b).^[185] 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.^[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,^[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,^[175,177,181] and the usage of protective interphases,^[178] might allow the use of Al metal as an anode in the near future.

Figure 20. Ragone plot of various ZIAB and AIAB electrodes using the data from Tables 1–5. Note that values for AIAB cathodes is based on various AIAB cathodes against TiO₂ anode. Data for Li-ion batteries are sourced from ref. [197].

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 β -MnO₂^[39] and 170 Wh kg⁻¹ for α -MnO₂^[42] as compared to other water-based competing systems such as aqueous Li batteries (50–200 Wh kg⁻¹),^[160,181,186,187] aqueous Na-ion batteries ($\approx$ 100 Wh kg⁻¹),^[10] lead–acid (30–50 Wh kg⁻¹), and vanadium redox-flow batteries (10–30 Wh kg⁻¹).^[188] Recent reports also suggest that energy densities of $\approx$ 105 Wh kg⁻¹ can be achieved in full-cell AIABs if TiO₂ (anode) and Na₃V₂(PO₄)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)O₂ (TM = Ni, Co, Mn), can deliver an energy density of $\approx$ 120–160 Wh kg⁻¹ and power density of 200–300 W kg⁻¹,^[8] β -MnO₂ as ZIAB cathode has been demonstrated to feasibly enable energy densities of $\approx$ 100–200 Wh kg⁻¹ and power densities of 100–10 000 W kg⁻¹.^[39] In the case of AIAB cathodes, Na₃V₂(PO₄)₃ when used against TiO₂ anode can deliver a high energy density of $\approx$ 150 Wh kg⁻¹ and power densities as high as $\approx$ 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.

Figure 21. Relationship between design parameters of electrode, electrolyte, and current collector and the challenges in ZIABs and AIABs.

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 H₂O 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),^[51,189] 2) providing structural support to the lattice

Figure 22. Speculated effects of water in electrodes: a) crystal water can increase the ionic channel size, b) partial desolvation occurring when ion channels are smaller than hydrated cation size, c) no desolvation of hydrated cation might occur if the ion channels are large.

framework for stable repeated (de)intercalation,^[39,51,189] 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.^[100,190–192] 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.”^[193] These dangling bonds arise from edge terminations of the repeating lattice of a crystalline active material, and are easily neutralized by chemisorbed H₂O molecules.^[193] 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.^[102,193]

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.

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