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Research Progress, Challenges, and Prospects of High Energy Density Aqueous Aluminum-Ion Batteries: A Mini-Review

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Among emerging rechargeable batteries, rechargeable aluminum-ion batteries (AIBs) stand out for their high specific capacities and the abundance of aluminum, positioning them as an attractive electrochemical energy storage option. Despite the superior electrochemical performance of non-aqueous AIBs, aqueous aluminum-ion batteries (AAIBs) have garnered extensive research interest for their low cost and enhanced safety. Yet, realizing high energy density in AAIBs poses significant challenges. This article systematically reviews strategies and recent advancements in cathodes, anodes, and electrolytes aimed at achieving high energy density in AAIBs. It concludes with a forward-looking perspective on the design of AAIBs with high energy density and prolonged cycle life, highlighting promising directions for future researches.

1. Introduction

Since its commercialization in 1991, lithium-ion batteries have been widely integrated into daily life, powering devices ranging from mobile phones and computers to vehicles, all thanks to their high specific capacity, excellent rate performance, and long cycle life.[1–3] However, the journey of lithium-ion batteries has been marred by challenges, including the scarcity of lithium resources and safety concerns.[4,5] Despite extensive research efforts aimed at mitigating these issues, the quest for a viable alternative ion battery remains pivotal.

In recent years, various novel ion batteries, such as sodium,[6] potassium,[7] zinc,[8] magnesium,[9] calcium,[10] and aluminum-ion batteries,[11] have gradually entered the spotlight. Among these, aluminum-ion batteries have garnered significant attention due to their distinct advantages. Firstly, aluminum's abundance in the Earth's crust far exceeds that of lithium, substantially alleviating resource constraints for battery production(Figure 1b). Owing to aluminum's relatively low atomic mass and the involvement of a three-electron transfer process during redox reactions, aluminum-ion batteries boast a higher specific capacity (2980 mAh g^{-1}) and volumetric capacity (8046 mAh cm^{-3}) than most other ions(Figure 1a), quadrupling that of lithium.[12–14] This, combined with aluminum's inherent

safety benefits stemming from its stable chemical properties, positions aluminum-ion batteries as a highly promising alternative in the quest for sustainable and safe energy storage solutions.

Unlike non-aqueous aluminum-ion batteries that utilize expensive and toxic ionic liquid electrolytes, AAIBs employ water-based electrolytes, boasting significant advantages such as low cost, high safety, and environmental friendliness.[15] Additionally, the high sensitivity of ionic liquids to air and moisture necessitates that the assembly process of non-aqueous aluminum-ion batteries be conducted in strictly controlled environments, inevitably increasing production costs, particularly for large-scale applications. In contrast, aqueous aluminum-ion batteries can be easily assembled under standard environmental conditions. However, AAIBs also face significant challenges, some of which are common in today's rechargeable aqueous batteries. For instance, the electrochemical stability window (ESW) of water is only 1.23 V under standard conditions, limiting the operational voltage range and leading to suboptimal performance, such as the low energy density of aqueous aluminum-ion batteries. Some challenges are unique to Al/Al^{3+} systems, such as the formation of a passivation layer on the aluminum surface, which hinders the reversible stripping/deposition of aluminum, increases internal resistance, and lowers the output voltage. The high charge density of Al^{3+} results in strong electrostatic interactions with cathode materials, including repulsion from metal cations and attraction to anions, affecting the diffusion kinetics of Al^{3+}. Despite being in the early stages of research, AAIBs face numerous challenges regarding electrodes and electrolytes.[16–19]

This review aims to provide a comprehensive overview of the key challenges and current research progress toward high energy density aqueous aluminum-ion batteries, focusing on cathodes, anodes, and electrolytes. By summarizing these challenges and advancements, this article hopes to offer valuable insights into the opportunities and challenges of high

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energy density aqueous aluminum-ion batteries and guide future research directions.

2. Constructing High-Energy-Density Aqueous Aluminum-Ion Batteries

To construct high energy density AAIBs, it is crucial to optimize the theoretical energy density of the battery, which can be mathematically represented as follows:

$$E = \frac{\text{Theoretical specofic capacity of the cathode (mAh/g)} \times \text{Average discharge voltage of the battery (V)}}{\text{Mass of the cathode material (g)} + \text{Mass of the anode material (g)}} \quad (1)$$

This formula elucidates that enhancing the energy density of AAIBs revolves around two fundamental criteria:

a) **High Specific Capacity of Electrode Materials**: Maximizing the battery's energy output necessitates the utilization of electrode materials with high specific capacities. This denotes the ability of the materials to store a maximum amount of electrical charge per unit mass. For cathode materials, it is pivotal to explore materials such as transition metal oxides, which not only possess high theoretical specific capacities but are also compatible with aluminum ion reactions. In the context of the anode, while aluminum inherently exhibits a high specific capacity, augmenting its practical utilization through surface modification and microstructural design is essential for elevating the overall energy density of the battery.

b) **Significant Redox Potential Difference Between Electrode Materials**: The discharge voltage of a battery is determined by the redox potential difference between the cathode and anode materials. Consequently, selecting a combination of electrode materials with a large potential difference can significantly increase the battery's energy output. In AAIBs, this implies not just selecting cathode materials with high oxidation potentials but also ensuring that the electrolyte possesses a sufficiently wide electrochemical window to support higher operational voltages, thereby enhancing the energy density.

Beyond these core conditions, the following factors must also be considered to optimize the performance of AAIBs:

a) **Selection of the Electrolyte**: The electrolyte should not only have a broad electrochemical stability window to support high voltage operation but also facilitate efficient aluminum ion transport while minimizing side reactions, such as hydrogen evolution.

b) **Optimization of the Electrode-Electrolyte Interface**: Employing interface engineering techniques to improve the electrochemical activity and stability of the electrode surface, as well as enhancing compatibility between the electrode and electrolyte, can effectively reduce interfacial impedance and enhance ion transport efficiency.

c) **Microstructural and Porosity Design**: The microstructural design and porosity of electrode materials play a crucial role in increasing the electrode-electrolyte contact area, enhancing ion diffusion rates, and shortening the electron transport path, all of which significantly improve the battery's energy density and power density.

Systematically exploring and integrating these strategies, developing high energy density aqueous aluminum-ion batteries is not only technically feasible but also holds significant application prospects in the realm of energy storage.

3. Selection of the Electrolyte

In the realm of AAIBs, the role of the electrolyte is paramount, especially in enhancing battery voltage by tweaking electrolyte compositions to extend the ESW and optimizing the aluminum ion deposition process, effectively mitigating the hydrogen evolution reaction (HER).
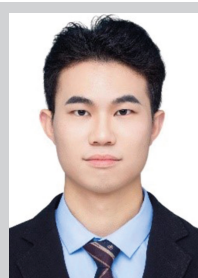
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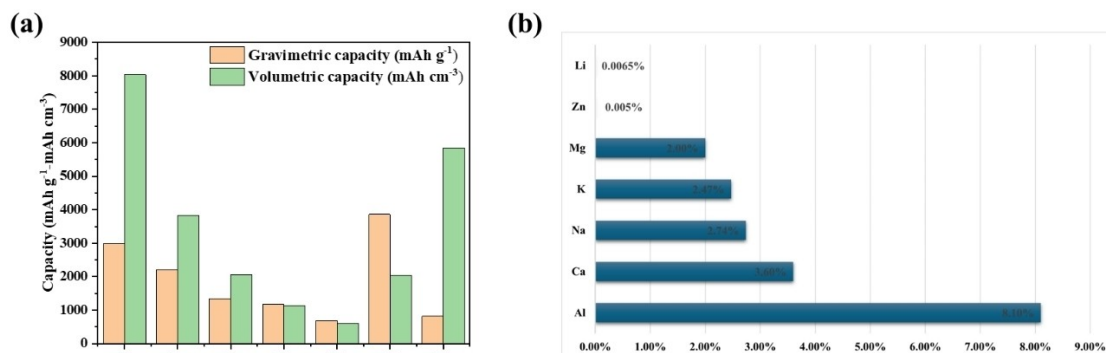
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Figure 1. a) Comparison of the gravimetric and volumetric capacities of various metals; b) Comparison of the abundance of various metals in the Earth's crust.

3.1. "Water-in-Salt" Electrolytes

Notably, the strategy of using "Water-in-salt" electrolyte (WISE) leverages specific high-concentration aluminum salts and their unique solvation structures to significantly suppress the activity of water molecules, thereby effectively broadening the ESW and facilitating reversible aluminum deposition and stripping. Despite the breakthrough achieved with 5 M $Al(OTF)_3$ WISE electrolytes in AAIBs, further modification of the electrolyte remains critically necessary. For instance, the addition of dihydrogen phosphate ($H_2PO_4^-$) can effectively alleviate the passivation issue of the Al anode, enhancing the battery's cycle stability.[20] The introduction of H_3PO_4 not only thins the passivation layer but also effectively prevents further formation of the passivation layer through interaction with $Al(TOF)_3$ (Figure 2a). Long-term stability assessments of mixed electrolytes have shown that electrolytes with added H_3PO_4 display much more stable polarization voltages, significantly extending the battery's lifespan (Figure 2b). Moreover, FTIR testing results have revealed that the expansion of the electrochemical window is primarily due to the coordination between hydrated Al^{3+} and phosphate oxygen (Figure 2c–2e). The complex cationic formation in hybrid electrolytes, $Al(H_2PO_4^-)_x(TOF^-)_y + (H_2O)_n$, effectively reduces the high charge density of Al^{3+}, inhibiting the formation of a passivation layer on the Al anode surface, thus enabling long life and high performance for the Al//PANI system. Furthermore, recent studies have found that adding polar pyridine-carboxylic acid to the aluminum trifluoromethanesulfonate aqueous solution optimizes the solvation structure of Al^{3+}, effectively suppressing water activity in the electrolyte, improving Al surface energy, preventing random aluminum deposition, and significantly enhancing the long-term electrochemical stability of the electrolyte.[21] These advancements not only offer significant reversibility and high energy density possibilities for aqueous aluminum-ion batteries but also provide important research directions and practical guidance for the future development of AAIBs technology.

However, despite the technological breakthrough of the $Al(OTF)_3$ WISE electrolyte, challenges related to its low solubility and production cost remain. In 2019, Pan and colleagues[22] discovered that reversible aluminum deposition and stripping could be realized in an ultra-concentrated aqueous solution of

$AlCl_3 \cdot 6H_2O$. Subsequently, an aqueous aluminum-graphite battery was successfully assembled, featuring an average discharge voltage of 1.44 V, an energy density of up to 220 Wh/kg, and demonstrating excellent cycling performance. This study not only signals a new direction for the further development of AAIBs but also holds great application value by utilizing low-cost $AlCl_3 \cdot 6H_2O$, significantly reducing the manufacturing cost of the battery.

3.2. Molecular Crowding Electrolytes

The "molecular crowding" approach, involving the adjustment of electrolyte composition to inhibit the hydrogen evolution reaction (HER), emerges as an effective strategy. This method integrates macromolecules, primarily of organic nature, that can form hydrogen bonds with water, thus reducing its reactivity and mobility. A study incorporating up to 94% polyethylene glycol (PEG) into the electrolyte of aqueous lithium-ion batteries demonstrated this approach, achieving a significant reduction in the onset potential of HER by 1.1 V (Figure 3a).[23] This not only broadens the selection of anode and cathode materials but also enhances the overall feasibility and operational voltage of aqueous lithium batteries. A similar methodology observed improvements in stability and cycle life in zinc-ion batteries, although, due to zinc's inherent potential aligning with HER, a significant increase in voltage was not achieved.[24]

Further emphasizing the versatility of the "molecular crowding" strategy, its application has been explored in the context of aluminum-air batteries. For instance, Lv et al.[25] significantly improved battery performance by integrating sodium polyacrylate (PANa) into the aqueous electrolyte. Compared to medium concentrations, high PANa concentrations (90–87%) documented a notable 80 mV increase in the ESW (Figure 3b). However, finding a balance is crucial as while elevated PANa concentrations suppress HER activity and lower the equilibrium potential E (Figure 3c), they also induce a sharp decline in conductivity, potentially impacting the final voltage from a kinetic perspective (Figure 3d). Therefore, an 87% PANa concentration was identified as the optimal balance.

Looking forward, integrating "molecular crowding" into AAIB systems will also necessitate a fine balance between
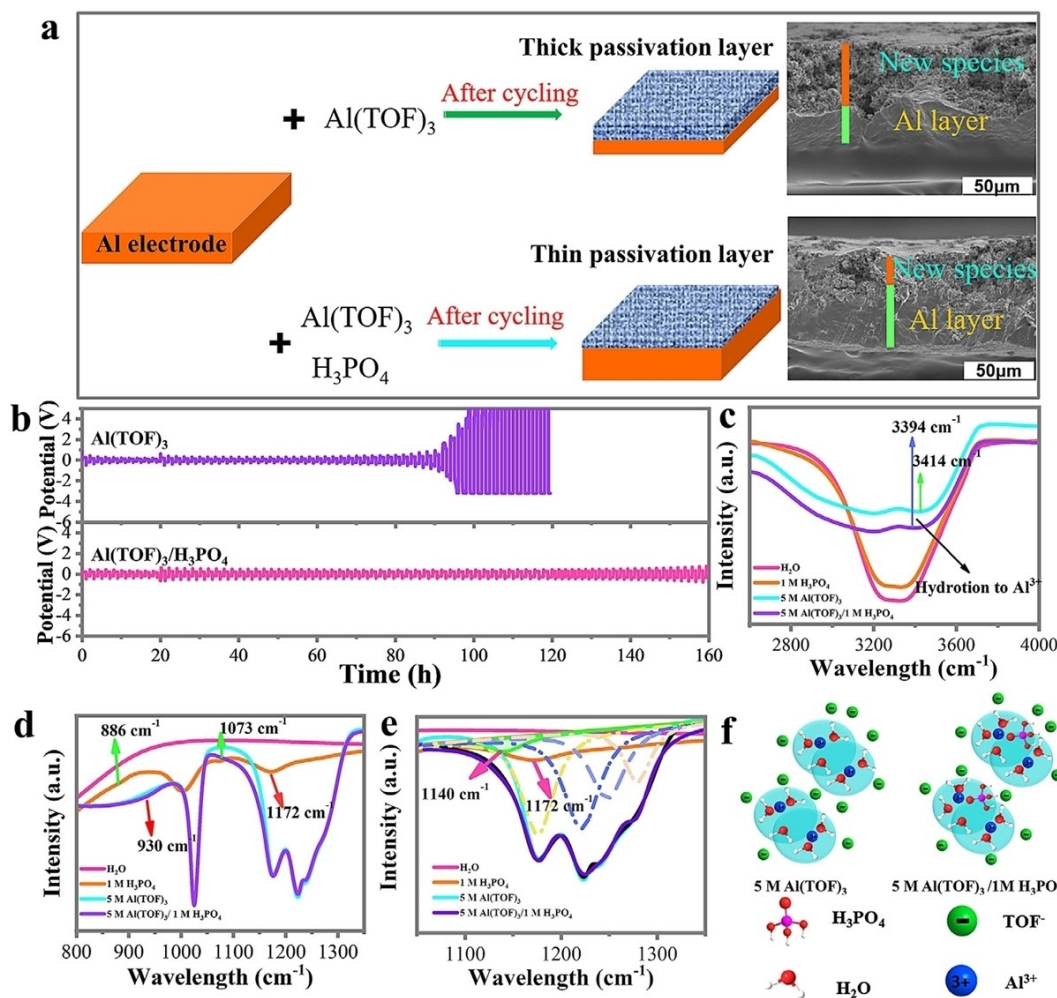
Figure 2. a) Schematic representation of passivation film formation by cycling in 5 M Al(TOF)$_3$ and 5 M Al(TOF)$_3$/1 M H$_3$PO$_4$ electrolytes. The inset is a cross-sectional SEM image of the Al anode after 100 cycles in the corresponding electrolyte; b) Al//Al symmetric cells tested in 5 M Al(TOF)$_3$ and 5 M Al(TOF)$_3$/1 M H$_3$PO$_4$ electrolytes at a current density of 1 mA cm^{-2}; c), d) and e) FTIR spectra of H$_2$O, 1 M H$_3$PO$_4$, 5 M Al(TOF)$_3$ and 5 M Al(TOF)$_3$/1 M H$_3$PO$_4$ solutions ; f) Schematic representation of the solvated states of 5 M Al(TOF)$_3$ and 5 M Al(TOF)$_3$/1 M H$_3$PO$_4$ electrolytes.[20] – Copyright 2021 Elsevier B.V.

enhancing conductivity and suppressing HER, alongside the careful selection of crowding agents highly compatible with aluminum. Additionally, certain electrolytes capable of disrupting hydrogen bonds to reduce water reactivity or forming protective layers on the aluminum anode surface can achieve the goal of enhancing energy density and cycle life. A study designed a semi-gel electrolyte consisting of polyethylene glycol (PEG) as the framework, aluminum perchlorate as the electrolyte adherent, and perchloric acid as an auxiliary regulator (PEG-Al@H).[26] It was found that a new interface, termed the Aluminum Electrolyte Interface (AEI), forms between the electrolyte and the aluminum anode during charging. The AEI, a protective layer formed by the polymerization of PEG during the aluminum ion desolvation process, inhibits fast kinetic reactions causing side reactions, prevents deep corrosion of the aluminum anode, and significantly enhances battery performance(Figure 4).

4. Selection of the Anode

To advance AAIBs towards the goal of higher energy density, it is imperative to meticulously select anode materials that possess high specific capacities and lower electrode potentials. Currently, anode materials commonly employed in AAIBs encompass MoO$_3$,[27–29] WO$_3$,[30] TiO$_2$,[31–34] aluminum metal and aluminum-based alloys.[35–38] Among these options, aluminum metal electrodes, owing to their lower standard electrode potential (−1.66 V) and their remarkable high specific capacity (2980 mAh g^{-1}) as well as volumetric capacity (8046 mAh cm^{-3}), are considered the optimal choice for anodes.[14, 39] However, employing aluminum as the anode material inevitably confronts the technical challenge of surface passivation on aluminum.

4.1. Modified Al foil

To bolster the electrochemical efficiency of aluminum anodes in aluminum-ion batteries (AIBs), the modification of surface layers
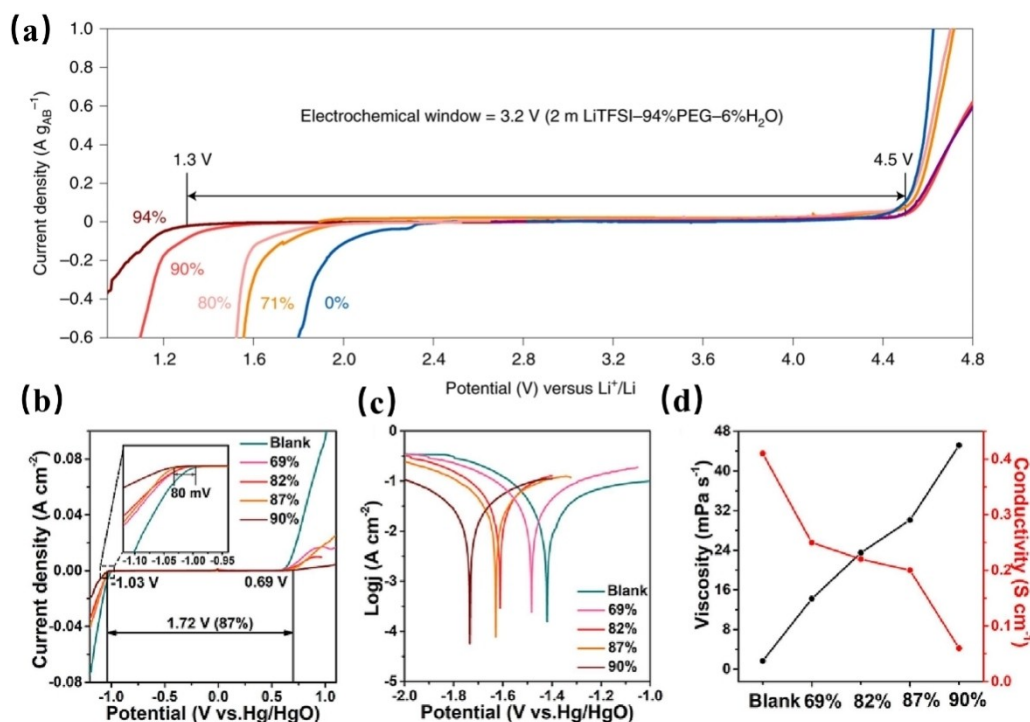
Figure 3. a) Electrochemical stability windows for $2\,M$ LiTFSI–xPEG–$(1-x)H_2O$ ($x = 0, 71, 80, 90, 94\%$) determined by LSV tests on AB-coated aluminium foil at a scan rate of $0.2\,mV\,s^{-1}$[23] – Copyright 2020 Springer Nature; b) The electrochemical stability windows of blank electrolyte (4 M KOH) and containing different concentrations of PANa; c) Polarization curves of aluminum anodes in Blank electrolyte (4 M KOH) and containing different concentrations of PANa; and d) Viscosity and conductivity of different electrolyte[25]. – Copyright 2021 Elsevier B.V.
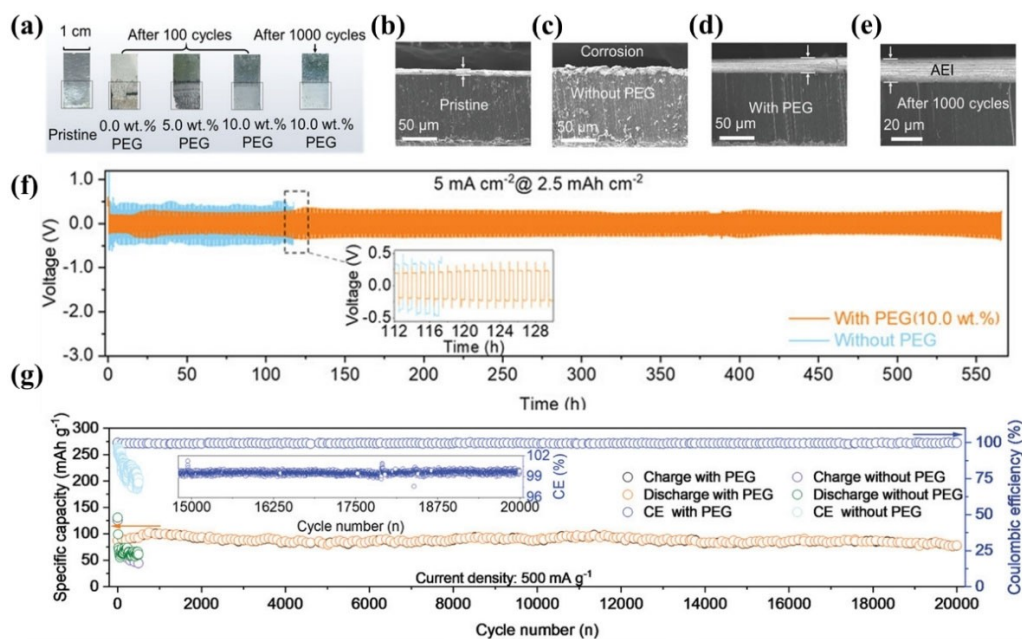

Figure 4. The evolution and characterization of Al electrolyte interface (AEI). a) The digital photos of Al anode before and after operation in electrolyte with different content of PEG; b–e) The cross-section SEM images of Al electrode before and after operation without PEG and with 10.0 wt% PEG after 1000 cycles; f) Long-term Al plating/stripping cycling of symmetric Al||Al batteries at $5\,mA\,cm^{-2}$ with a capacity of $2.5\,mAh\,cm^{-2}$; g) Cycling performance of the full-cell with PEG and without PEG at $500\,mA\,g^{-1}$[26]. – Copyright 2023 John Wiley and Sons.

through composition and microstructure adjustment is pivotal. This approach not only aims at the surface treatment of aluminum anodes but also focuses on the construction of a protective layer to curtail self-corrosion – a critical step towards elevating the performance of AIBs.

Advancements in AIB performance through surface modification reveal a strategic evolution from mere treatment to sophisticated protective design:

a) **Electropolishing for Enhanced Performance**: In addressing the quest for improved recyclability and performance, the shift towards electropolished aluminum electrodes emerges as a breakthrough.[40] Unlike their pristine and etched counterparts, these electrodes showcase remarkable performance with substantial capacity retention across an extensive cycle life of 10,000 cycles, highlighting a strategic move towards enhancing electrochemical properties.

b) **Corrosion Inhibition through PVDF Coating**: The development of a polyvinylidene fluoride (PVDF) coating responds to the critical challenge of corrosion. By forming strong F—Al bonds, this coating not only inhibits the formation of corrosive species but also promotes uniform aluminum deposition, thereby significantly boosting the coulombic efficiency and presenting a solution to corrosion challenges.[41]

c) **Amorphization Strategy for Activation**: The innovative amorphization of metallic aluminum anodes introduces a porous amorphous aluminum interlayer (Figure 5a). This strategic development reduces the nucleation energy barrier and facilitates ion deposition, effectively addressing passivation issues and enhancing the electrochemical performance and longevity of AIB cells.[42]

d) **Ultrathin Interfacial Layer for Stability**: The creation of an ultrathin aluminum interfacial layer (AIL) emerges as a solution to dendritic growth, ensuring dendrite-free aluminum plating and peeling (Figure 5b). This approach not only leads to high efficiency and stability but also marks a significant step towards achieving reversible aluminum plating/stripping at high area capacities.[43]

e) **Effective Surface Area Enhancement**: By designing an anode with an increased effective surface area and stable electrode/electrolyte interface, uniform aluminum electrodeposition is facilitated (Figure 5c). This strategy significantly enhances the cell stability and specific capacity, demonstrating the importance of interface design in improving electrochemical performance.[44]

f) **MXene Layer for Protection and Longevity**: The application of an ultrathin MXene layer to the aluminum surface exemplifies the protective armor concept, offering high ionic conductivity and mechanical flexibility(Figure 5d). This layer enables the anode to support a high current density while maintaining full capacity retention over an extended cycle life, highlighting the role of advanced materials in protective design.[45]

While the development of protective layers on aluminum foil surfaces stands as a formidable defense against oxidation, the exploration of their stability and interaction with various electrolytes remains crucial. Delving into these aspects is essential for the continued optimization and enhancement of aluminum anode performance in AIBs, underscoring the interconnected advancements in surface modification strategies.

4.2. Al Alloys

Alloying aluminum with other metals addresses critical challenges in battery technology, such as passive oxide layer formation, hydrogen precipitation, and self-corrosion, paving the way for more durable and efficient energy storage solutions. To mitigate surface-related issues like dendrite growth and corrosion, which compromise battery life and safety, the integration of key kinetic parameters was explored. This exploration led to the development of a stable porous aluminum structure, significantly enhancing the performance of AAIB.

In pursuit of solutions to dendrite formation and corrosion – a common pitfall for solid-state Al anodes – a novel approach involving liquid Ga anodes was introduced.[46] This strategy leverages the reversible alloying/dealloying capabilities between Al and Ga, effectively circumventing these longstanding issues. Further advancements were achieved by employing aluminum-copper lamellar heterostructures as active anode materials.[47] This design not only improved electrochemical reversibility but also provided a dendrite-free environment during the crucial stripping/plating cycles.
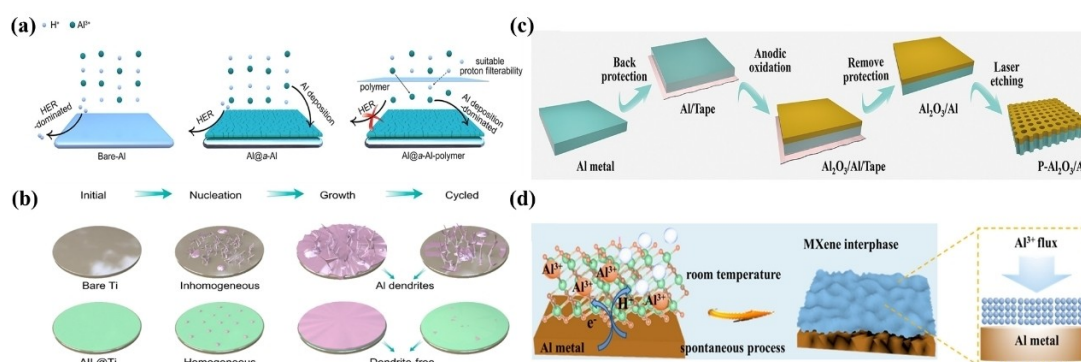

Figure 5. a) Schematic illustration for improving the reversibility of Al plating/stripping using the proton-filtering polymer film[42] – Copyright 2022 American Chemical Society; b) Schematic illustration of Al plating/stripping behaviors with and without AIL[43] - Copyright 2023 American Chemical Society; c) Structural diagram and preparation flowchart of P-Al$_2$O$_3$/Al anode[44] – Copyright 2023 Elsevier B.V.; d) Structural diagram and preparation flowchart of P-Al$_2$O$_3$/Al anode[45] - Copyright 2023 American Chemical Society.

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Exploring different alloy compositions, a Zn-Al alloy anode demonstrated exceptional reversibility and specific capacities in mixed electrolytes.[48] This finding indicated a significant leap towards enhancing the cycle life of AAIBs. Additionally, the integration of iron content into aluminum alloy anodes emerged as a strategy to minimize surface corrosion, thereby extending battery life further.[49]

A noteworthy innovation came with the development of Sn-Al laminate electrodes.[50] These electrodes showcased a remarkable reduction in internal resistance, alongside improved cycling stability, indicating a promising direction for full-cell applications. Each of these alloying strategies not only addresses specific issues inherent to aluminum anodes but also underscores a cohesive approach towards developing scalable, cost-effective, and high-performance AAIBs. Collectively, these advancements signify a strategic push towards refining anode stabilization techniques, marking a pivotal step towards the commercial viability of AAIB technology.

5. Selection of the Cathode

To achieve high energy density in aqueous aluminum-ion batteries, not only is the selection of aluminum metal as the anode crucial, but the choice of appropriate cathode materials is also paramount. The cathode typically represents a critical component of the battery, and the ideal cathode material should exhibit a high capacity, elevated working potential, structural stability, and good electrical conductivity. The cathode materials currently reported to fulfill the requirements for constructing high-energy-density aqueous aluminum-ion batteries primarily include manganese oxides, Prussian blue analogs (PBAs), graphite and some Organic compounds. Various AAIB cathode materials that can achieve high energy density are summarized in Table 1

5.1. Manganese Oxides

The exploration of manganese oxides as a key component in AAIBs represents a concerted effort to leverage their adaptable

structures and valence flexibility for improved battery performance. These efforts have collectively addressed the challenges of energy density, capacity, and stability within AAIBs through innovative approaches to material transformation and electrolyte interaction.

The initial breakthrough came with the discovery that α-MnO_2,[38] due to its structural and valence adaptability, could support diffusion-dominated transport mechanisms, as revealed through cyclic voltammetry studies. This foundational insight led to the development of a full cell configuration combining TAl, 2 M $Al(OTF)_3$, and α-MnO_2, which achieved an impressive capacity of 380 mAh/g and a discharge plateau of 1.3 V, translating into an energy density of 500 Wh/kg.

Building upon this foundation, the technique of in-situ electrochemical reformation within a water-in-salt electrolyte containing $AlCl_3$ and $MnSO_4$ was introduced (Figure 6a–d). This approach facilitated a dual-stage transformation of α-MnO_2 nanowires into $AlMnO_2$ nanospheres, through a process that enabled the reversible intercalation and deintercalation of Al^{3+} ions, resulting in a battery that boasted a 1.9 V discharge plateau and a capacity of 285 mAh/g at a high current density.[51]

Further research into the reaction mechanisms involving birnessite MnO_2 revealed a cyclic process where the reduction of MnO_2 to soluble Mn ions and the oxidation of TAl to Al^{3+} led to the formation of an amorphous Al-Mn—O layer on the cathode, alongside Al plating on the anode. This finding highlighted the reversible nature of this process, showcasing the potential of utilizing both Al^{3+} and Mn ions as charge carriers to enhance battery reversibility.[58]

In another advancement, the electrochemical transformation of spinel Mn_3O_4 (Figure 6e) into a layered Al-Mn-O-H_2O structure was achieved, emphasizing the role of Al^{3+} ions and crystal water in reducing electrostatic interactions, thereby enhancing the battery's overall performance.[59] The $Al_{2/3}Li_{1/3}Mn_2O_4$ (ALMO) cathode material, which also has a spinel structure, has been found suitable for use in aqueous aluminum-ion batteries. Al^{3+} ions can be reversibly extracted and inserted into the ALMO cathode material through the oxidation and reduction of Mn. The full battery prepared with the ALMO cathode demonstrates a high energy density of 183 Wh kg^{-1}

Table 1. Summarization of electrochemical performance of high energy density cathode materials for AAIBs.

Cathode	Anode	Electrolyte	Initial capacity (mAh g^{-1})	Voltage range (V)	ref
α-MnO_2	TAl	2 M $Al(OTF)_3$	380	0.5–2	[38]
Al_xMnO_2	Al	$AlCl_3$ and $MnSO_4$	285	0.6–2	[51].
$Al_xMnO_2 \cdot nH_2O$	Al	5 M $Al(OTF)_3$	467	0.5~1.8	[35]
$Al_{2/3}Li_{1/3}Mn_2O_4$	Pt	1 M $AlCl_3$/NaCl	151.8	0~1.16 (vs. Ag/AgCl)	[52]
defective MnFe-PBA/	IL-treated Al	1 M $Al(OTF)_3$	64.7	0.6~1.75	[53]
CoHCF	Al	saturated $AlCl_3$	103.5	−0.2~1.1(vs.SCE)	[54]
graphite	Al	$AlCl_3 \cdot 6H_2O$	165	0.8~2.5	[22]
carbon decorated graphene	Pt wire	1 M AlCl3	152.7	0.3~0.9 (vs.Ag/AgCl)	[55]
calix[4]quinone	IL-treated Al	1 M $Al(OTF)_3$	333	0.4~1.4	[56]
PTMA	Al	1 M $Al(OTF)_3$	115	0.8~1.7	[57]

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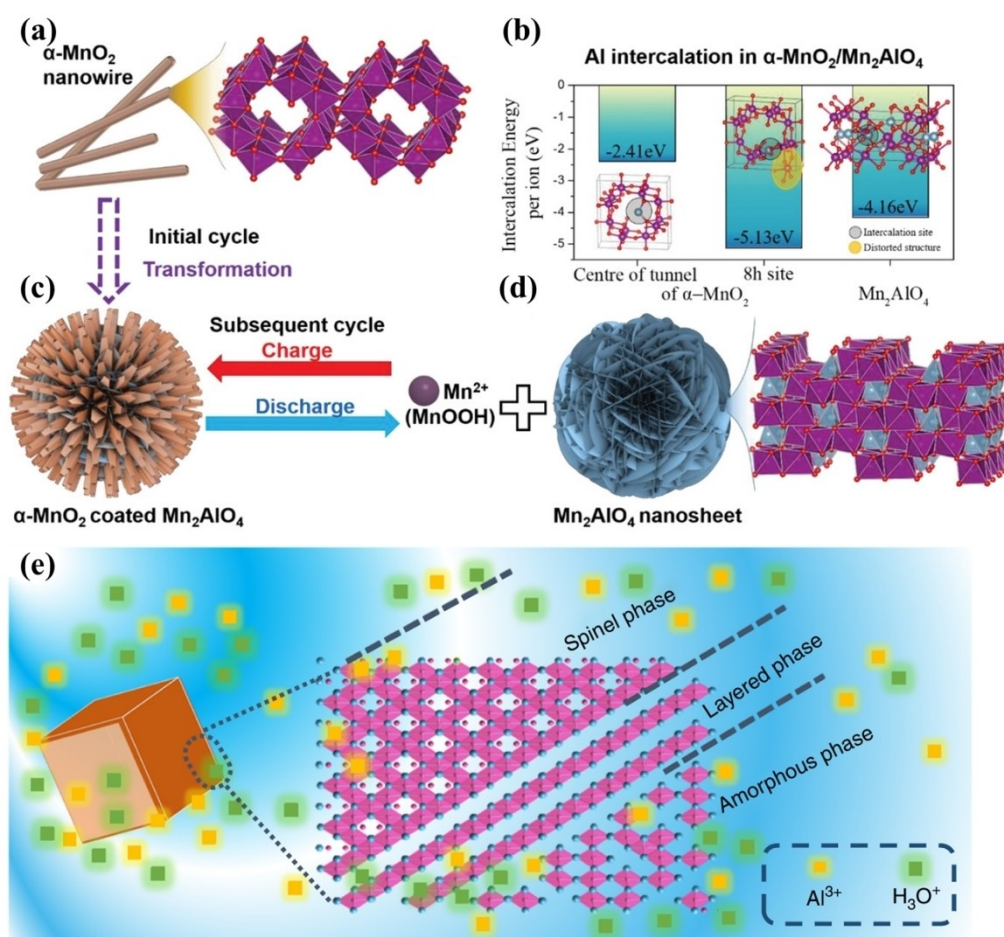Societies Publishing

Figure 6. Schematic diagram of the transformation of MnO_2 during cycling: from α-MnO_2 nanowire to Al_xMnO_2 nanosphere, including simulation results. a) Pristine α-MnO_2 nanowire. b) Insertion energies for α-MnO_2 and Mn_2AlO_4 with Al insertion. c) Electrochemically reformed Al_xMnO_2 nanosphere and its interior structure. d) Mn_2AlO_4 nanoflower[51] – Copyright 2021 John Wiley and Sons; e) Schematic profile of the mixed-phase structure of $Al_xMnO_2\cdot nH_2O$[59] – Copyright 2019 Springer Nature.

and an average operating voltage of about 1.31 V, making it a promising candidate for large-scale energy storage applications.[52]

A significant transformation strategy involved the conversion of cubic MnO to Al_xMnO_2 through a two-electron redox mechanism. This strategic adjustment not only facilitated the rearrangement of Mn into the MnO_2 phase but also supported the seamless insertion of Al^{3+}, leading to a marked increase in capacity to 460 mAh/g over 80 cycles.[35] The $Al_xMnO_2\cdot nH_2O$ anode material, formed by the topological transformation of MnO, allows Zn^{2+} ions to be embedded into its spinel structure, providing structural stability. Combined with a Zn-Al alloy anode, it delivers a discharge plateau of 1.6 V. The first-cycle discharge capacity reaches 554 $mAh\,g^{-1}$, and a high capacity of 313 $mAh\,g^{-1}$ is maintained after 100 cycles.[60]

These collective advancements underscore a pivotal theme: the critical interplay between the structural and chemical adaptability of manganese oxides, the dynamics of aluminum ions, and the chemistry of the electrolyte system. This synergy has paved the way for the development of AAIBs with superior capacities, voltage platforms, and energy densities, illustrating

the profound impact of material science innovations on the evolution of battery technologies.

5.2. Prussian Blue Analogs

In the quest to enhance the energy density and efficiency of AAIBs, the exploration and innovation in PBAs as cathode materials have marked significant strides.[61] The journey began with the utilization of copper hexacyanoferrate (CuHCF),[62] which set a foundational understanding of ion shielding and intercalation capabilities (Figure 7a) Progressing from this point, the development of more sophisticated compounds such as $K_{0.2}Fe[Fe(CN)_6]_{0.79}\cdot 2.1H_2O$[63] and $K_{0.02}Ni_{1.45}[Fe(CN)_6]\cdot 2.6H_2O$[64] introduced by subsequent research, underscored the critical role of double and mixed redox centers. These advancements not only achieved higher discharge capacities but also underscored the importance of maintaining stability through numerous battery cycles.

The application of defect engineering to MnFe-PBA cathodes[53] emerged as a breakthrough, enhancing reaction kinetics by promoting rapid diffusion of Al^{3+} ions. This
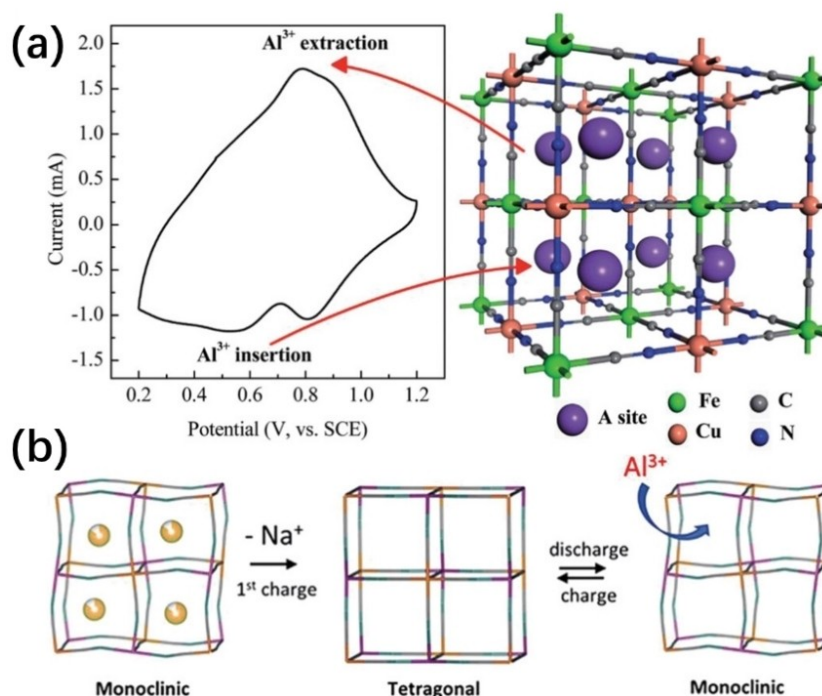
Figure 7. a) Typical CV curve of the CuHCF electrode in 0.5 M $Al_2(SO_4)_3$ aqueous solution at the scan rate of 1 mV s^{-1} and the schematic positions of Al^{3+} in the CuHCF framework[62]. – Copyright 2015, Royal Society of Chemistry. b) Schematic illustration of structural evolution in NMHCF upon cycling[65]. – Copyright 2020 American Chemical Society.

innovation, achieved through creating expanded ion transport channels and reducing Coulombic interactions, was further validated by the active role of Mn and Fe ions in the electrochemical process, thereby boosting discharge capacities and voltages. Similarly, the introduction of $Na_{1.68}Mn[Fe(CN)_6]\cdot 1.7H_2O$ (Figure 7b) with dual transition metal centers showcased an initial high energy density, illustrating the delicate balance between structural integrity and electrochemical performance over extended cycles.[65]

A notable contribution from our research group involved the development of nano-cubic cobalt hexacyanoferrate (CoHCF), representing a significant leap in cathode material

performance for AAIBs.[54] Employing metallic aluminum as the anode and a saturated $AlCl_3$ electrolyte, this system adeptly managed the intercalation and de-intercalation of Al^{3+} ions, alongside a minor participation of H^+ ions, during the electrochemical cycles (Figure 8). The ability of CoHCF to catalyze the reversible redox reactions of $Cl^{<M->}/Cl^0$ at higher potentials not only achieved impressive specific capacities and redox potentials but also demonstrated a battery system with an average discharge voltage of 1.56 V and an energy density reaching 155 Wh kg^{-1}, paired with remarkable rate performance and cycle stability.
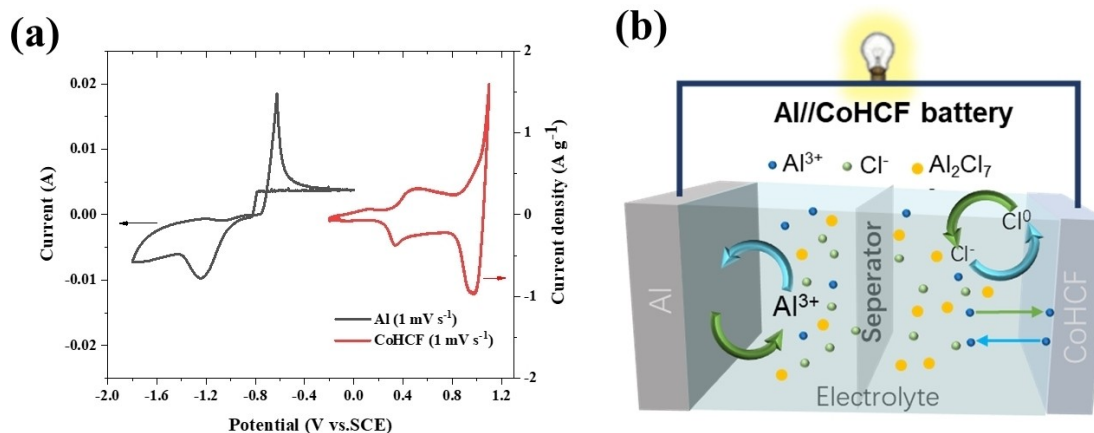

Figure 8. Working principle and CV curves Al//CoHCF battery: a) CV curves of Al and CoHCF electrodes in saturated $AlCl_3$ aqueous solution (1 mV s^{-1}); and b) schematic diagram of working principle of Al//CoHCF battery.[54] – Copyright 2023 Wiley VCH.

Collectively, these developments illuminate the pathway towards optimizing AAIB technologies, highlighting the potential of PBAs in revolutionizing energy storage solutions. The ongoing research and innovation in this field suggest a promising avenue for further enhancements, aiming to fully realize the application potential and economic value of high-energy-density AAIBs.

5.3. Graphite

Graphite emerges as a pivotal cathode material in the advancement of aqueous aluminum-ion batteries (AAIBs), attributing to its profound electrochemical performance and structural stability.[55] In the quest to overcome the challenges presented by the low standard reduction potential of Al^{3+} in aqueous solutions, graphite offers a viable solution, owing to its high electrical conductivity and the ability to facilitate rapid ion intercalation and de-intercalation. Graphite, paired with a "water-in-salt" $AlCl_3 \cdot 6H_2O$ electrolyte, revolutionizes aqueous aluminum-ion batteries (AAIBs) by enhancing their electrochemical stability window to about 4 V and overcoming the challenge of Al-ion's low standard reduction potential in water. This synergy enables rapid ion intercalation and de-intercalation within the graphite cathode, leading to a high-performing AAIB that boasts a capacity of 165 mAh g^{-1} at 500 mA g^{-1} with over 95% Coulombic efficiency over 1000 cycles.[22] This system not only demonstrates improved energy density and operational stability but also offers cost efficiency and safety through dendrite-free operation. The dual-ion intercalation process, verified by advanced analytical techniques, along with cyclic voltammetry analyses, further confirm the electrolyte's role in extending the battery's electrochemical stability and ensuring uniform aluminum deposition. This graphite-based AAIB marks a significant step towards sustainable, high-energy-density, and economically viable battery technologies, laying the groundwork for future advancements in the field.

5.4. Organic Compounds

Research has optimized macrocyclic calcium[4]quinone (C4Q)[56] with large cavities and multiple adjacent carbonyl structures from six quinone compounds, making it an excellent cathode material for high energy density AABs. Using Al as the anode and a 1 M aluminum triflate (Al(OTF)$_3$) aqueous solution as the electrolyte (Figure 9a), the battery demonstrates a high capacity of 400 mAh g^{-1}, high-rate capability (300 mAh g^{-1} at 800 mA g^{-1}), and excellent low-temperature performance (224 mAh g^{-1} at $-20\,°C$). Combined experimental and theoretical calculations show that the Al(OTF)$_2^+$ cations coordinate with the carbonyl groups of C4Q during discharge, reducing desolvation penalties. Furthermore, the prepared Al–C4Q pouch cell exhibits an energy density of 93 Wh kg^{-1}, indicating its significant potential for large-scale applications. This work is expected to promote the use of organic cathodes in automated batteries.

2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO) and other nitroxyl radicals are typical organic electrode materials with high redox potential and fast electrochemical kinetics, widely used as cathode materials in multivalent metal-ion batteries. Research has investigated the electrochemical behavior of TEMPO in both organic and aqueous Lewis acid electrolytes. Through in-situ electrochemical characterization and theoretical calculations, it was revealed that TEMPO undergoes an irreversible disproportionation process in organic Al(OTF)$_3$ electrolyte, which can be transformed into a reversible process when switched to an aqueous medium. In the latter case, rapid hydrolysis and ligand exchange between [Al(OTf)$_3$TEMPO]$^-$ anions and water enable the overall reversible electrochemical redox reaction of TEMPO. These findings led to the design of the first flame-retardant and air-stable radical polymer aqueous AIB, providing a stable voltage output of 1.25 V and a capacity of 110 mAh g^{-1} over 800 cycles, with a per-cycle loss of 0.028% (Figure 9b).[57]
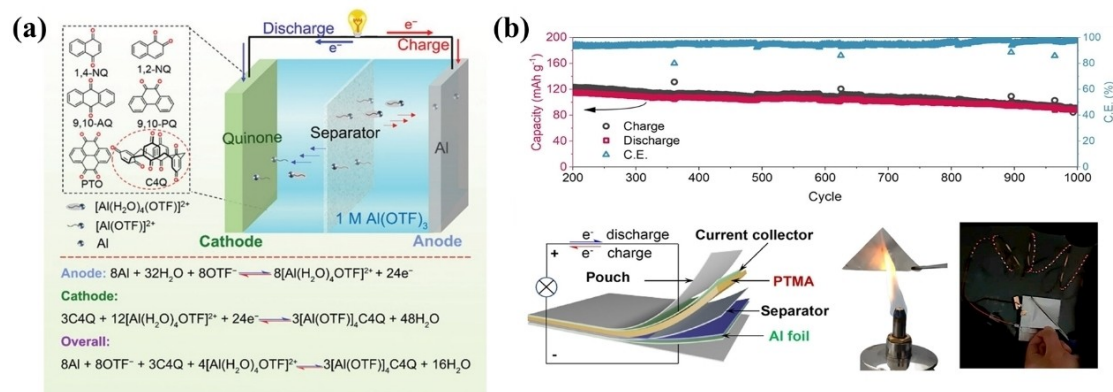

Figure 9. a) Schematic illustration of fabricated aqueous Al-quinone batteries.[56] – Copyright 2021 Wiley VCH; b) Long-term cycling performance and Coulombic efficiency of PTMA-based AAIBs at 4 C, along with the structure of soft-pack AAIBs (2.25 cm^2) demonstrating flame retardation and air stability[57] – Copyright 2023 American Chemical Society.

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6. Conclusion and Outlook

The trajectory of AAIBs from conceptualization to becoming a potential cornerstone for next-generation energy storage solutions epitomizes the confluence of innovation, scientific inquiry, and the imperative for sustainable alternatives. This comprehensive review delineates the evolution of AAIBs, anchored in a multifaceted approach addressing pivotal aspects such as cathode and anode material selection, electrolyte refinement, and the surmounting of intrinsic electrochemical challenges. The attributes of AAIBs, characterized by the utilization of abundant materials, inherent safety, eco-friendliness, and elevated energy densities, position them as a formidable contender against traditional lithium-ion batteries.

The exhaustive investigation into cathode materials, encompassing manganese oxides, PBAs, and graphite, underscores the persistent endeavor to enhance energy storage capacities whilst ensuring compatibility with aluminum ions. These endeavors have not only broadened the operational parameters and energy densities of AAIBs but also facilitated a nuanced understanding of the complex interactions between electrode materials and electrolytes. Similarly, advancements in anode materials, ranging from modified aluminum foils to novel aluminum alloys, signify a strategic pivot towards augmenting electrochemical efficiency, stability, and reversibility.

Electrolyte innovation, especially via "water-in-salt" and "molecular crowding" methodologies, has emerged as a pivotal mechanism in extending the electrochemical stability window, enabling efficient ion transport, and attenuating side reactions. These breakthroughs have appreciably expanded the operational voltage range and energy density of AAIBs, highlighting the electrolyte's critical role within the overarching battery architecture.

However, the challenge of directly evidencing aluminum deposition on the anode, primarily due to the difficulty in distinguishing newly deposited aluminum from the pre-existing substrate, further complicates the analysis. Precise elucidation of the operational reaction mechanisms necessitates the deployment of advanced in situ characterization techniques and experimental paradigms. These approaches are poised to be at the forefront of future research efforts, albeit extending beyond the purview of the current discourse.

Looking forward, the research and development horizon for AAIBs appears vast and promising. Future exploratory domains include the further amplification of energy density via material innovation, addressing scalability in production processes, and ensuring long-term stability and recyclability. The incorporation of novel materials and nano-engineering strategies holds the promise of unlocking superior capacities and energy efficiencies. Furthermore, an advanced understanding of interfacial phenomena between electrodes and electrolytes could catalyze the development of more robust and efficient battery systems.

As the global energy landscape progressively shifts towards greater sustainability, the role of AAIBs in facilitating renewable energy integration, grid stabilization, and powering emergent electronic devices grows increasingly pivotal. The journey hitherto has established a solid foundation, yet the path ahead necessitates ongoing innovation, collaboration, and an unwavering dedication to sustainability. The future of AAIBs, fueled by continuous research and technological advancements, not only promises to cater to the escalating demand for energy storage but also to contribute towards a more sustainable and electrified future.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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