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ARTICLE

Beyond Water: A Mini Review on Hybrid Electrolyte Strategies for Advanced Aqueous Aluminum Batteries

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Aqueous aluminum metal batteries (AAMBs) are considered a highly promising technology for future sustainable energy storage due to their high theoretical capacity, low cost, and environmental compatibility. However, achieving highly reversible and fast reaction kinetics remains a critical challenge that limits their advancement. In this perspective article, we argue that water-organic hybrid electrolytes (WOHEs) possess distinct advantages in concurrently optimizing the performance of both the anode and cathode in AAMBs through modifying the solvation structure and/or suppressing water activity. Finally, we highlight the necessity of in-depth investigations into the regulatory mechanisms of WOHEs on the electrochemical behavior at the electrode/electrolyte interface, particularly the formation of the solid electrolyte interphase (SEI) on the anode/cathode surface. Addressing these key aspects will facilitate the development and practical deployment of AAMBs.

1. Challenges and Enhancement Approaches for Aluminum Anodes in Aqueous Electrolyte Systems

Although lithium-ion batteries dominate the current energy storage market and remain a focal point in research, their widespread application in large-scale energy storage systems is hindered by high manufacturing costs and the inherent flammability risks associated with organic electrolytes.[1] As a result, aqueous batteries have gained increasing attention as a promising alternative due to their intrinsic safety and environmental sustainability.[2,3] While various intercalation-type anodes, such as molybdenum-based oxides, copper-based oxides, titanium-based oxides or sulfides, and composite carbides, offer high structural stability and can effectively avoid the dendrite formation associated with metal anodes, their performance is limited by the strong electrostatic forces that must be overcome during ion insertion and extraction. This leads to sluggish ion diffusion kinetics, which in turn restricts the full cell's rate capability.[4,5] In contrast, metal-based anodes exhibit rapid reaction kinetics during charging and discharging processes by plating/striping.[6] Additionally, metal anodes offer significantly higher theoretical capacities compared to conventional intercalation anodes,[7] and their straightforward fabrication process further reduces manufacturing complexity. Therefore, plating/striping-type metal anodes are more suitable for achieving high energy density and cost efficiency in battery systems.[6,8]

Among various metal anodes, aluminum stands out due to its high theoretical specific capacity (2,980 mA h g^{-1}) and a theoretical volumetric capacity (8,048 mA h cm^{-3}) surpassing that of lithium metal.[9,10] Moreover, aluminum is the third most abundant element and the most abundant metallic element in the earth's crust, making it readily available and economically viable.[10-12] When compared with several common metal anodes present in aqueous batteries, aluminum exhibits the lowest redox potential (-1.67 V vs. standard hydrogen electrode), which serves as a prerequisite for attaining high energy density in full cells. Owing to these advantages (Fig. 1a), aluminum metal batteries have emerged as a promising candidate for large-scale energy storage applications. Since 1855, when Hulot initially put forward the concept of aluminum batteries, the utilization of aluminum in the field of electrochemistry has commenced. In 2015, Dai's team achieved a significant breakthrough in the domain of rechargeable aluminium-ion batteries (AIBs). The battery they developed used $AlCl_3$/[EMIm]Cl ionic liquid (IL) electrolyte, and following 7,500 cycles, the capacity exhibited nearly no degradation.[13] Compared with the more mature ILs-based electrolyte, aqueous-based aluminum metal batteries (AAMBs) are still in their infancy. Although the aluminum anode in $Al(OTf)_3$-based aqueous electrolyte has demonstrated the ability to undergo plating and stripping reactions,[14] the short cycle life (typically fewer than 100 cycles) and the inability to achieve stable deposition at capacities exceeding 1 mA h cm^{-2} indicate that AAMBs face significant challenges in practical applications.[15-17] These challenges include (Fig. 1b): (a) The inherently poor

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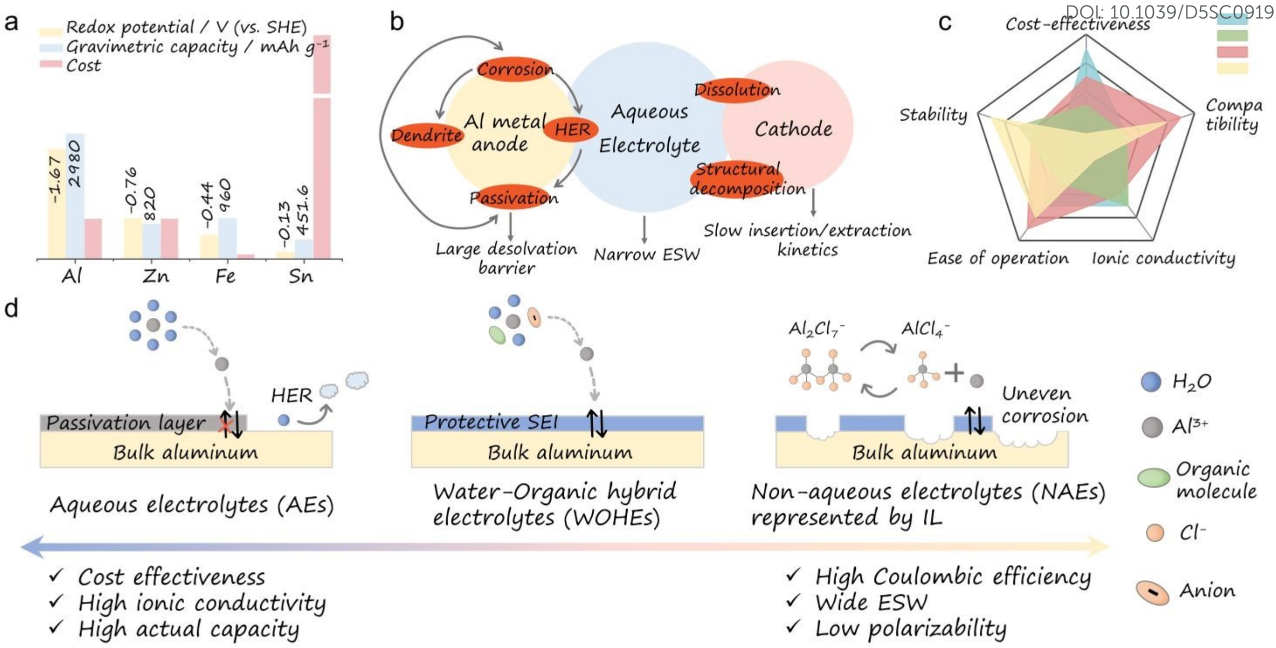

Fig. 1 Comparative analysis of aluminum metal batteries. (a) Comparison of commonly used aqueous-based metal anodes. (b) The challenges confronting AAMBs. (c) A systematic comparison of common modification approaches (Blue: Artificial SEI; Green: Substrate modification; Red: Electrolyte engineering; Yellow: High-concentration electrolyte). (d) Diagram illustrating the advantages and challenges of various electrolyte systems.

thermodynamic stability of the Al metal, which is prone to oxidation upon exposure to air or moisture, leading to the formation of an electrochemically inert aluminum oxide (Al_2O_3) layer that hinders subsequent electrochemical processes. (b) The susceptibility of Al metal to severe hydrogen evolution reaction (HER) and corrosion in aqueous electrolytes (AEs), resulting in the continuous consumption of both the active Al and the electrolyte, thereby significantly compromising the cycling stability and electrochemical performance of AAMBs. (c) Due to its smaller ionic radius and significantly higher charge density, Al^{3+} exhibits stronger Lewis acidity compared to common metal cations used in aqueous batteries. This characteristic results in a strong coordination interaction between Al^{3+} and water molecules, leading to a high degree of solvation.[18,19] Consequently, electrochemical processes such as desolvation and charge transfer are hindered, which represents a key limitation in enhancing the rate capability of Al-based full cells. (d) The strong electrostatic interactions also cause repeated insertion and extraction of Al^{3+} into the intercalation cathode, posing significant challenges to the structural stability of the cathode lattice.[20,21]

Therefore, to advance the widespread application and development of AAMBs, various strategies have been proposed to address these challenges, including substrate modification,[22,23] artificial solid-electrolyte interphase (SEI) construction,[14] electrolyte engineering,[19,24] and the incorporation of functional additives[25]. The electrolyte facilitates ion conduction between the positive and negative electrodes and the solvation structure within the electrolyte can directly influence the electrochemical reaction behaviors at the electrode-electrolyte interface (EEI). Consequently, electrolyte modification strategies offer a viable approach to simultaneously address inherent challenges associated with both the anode and cathode (Fig. 1c).

Although aluminum metal batteries (AMBs) based on ILs or other organic systems can effectively mitigate passivation and HER associated with AEs, their high cost, significant environmental sensitivity, and elevated viscosity constrain their practical applicability in grid-scale energy storage.[24] For instance, in conventional IL-based electrolytes employed in AMBs, aluminum is susceptible to corrosion induced by chloride complexes present in the electrolyte, leading to pulverization and structural disintegration.[19] Furthermore, Al^{3+} does not directly participate in electrochemical reactions but instead in the form of Al–Cl complexes in such systems, which significantly limits the utilization efficiency of Al atoms and consequently reduces the battery's practical capacity.[26] To address these limitations, inspired by the development of additives and eutectic electrolytes, in 2022, Xiao *et al*. designed a hydrated eutectic electrolyte consisting of $Al(ClO_4)_3·9H_2O$ and succinonitrile (SN).[19] This electrolyte system exhibited high safety and effectively inhibited water decomposition before Al deposition. Subsequently, the water-organic hybrid electrolytes (WOHEs) have garnered increasing attention in AAMBs. The incorporation of water not only mitigates the drawbacks associated with traditional non-aqueous electrolytes (NAEs) but

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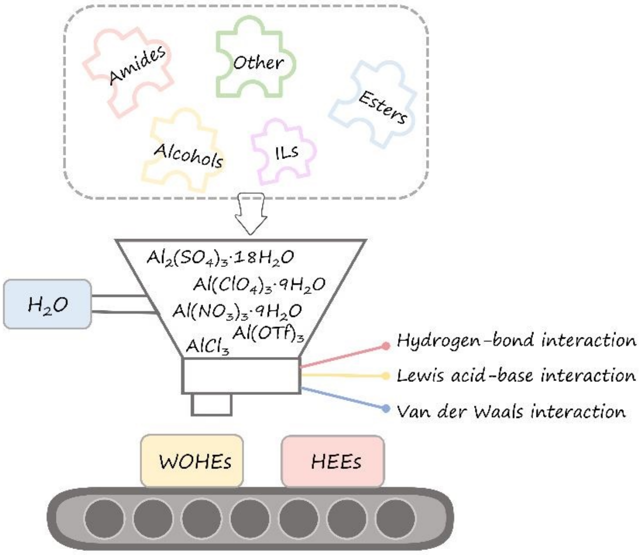

Fig. 2 Formation mechanism of WHOEs.

also modifies the solvation shell structure of aluminum ions, thereby enhancing ionic transport kinetics. Additionally, the organic constituents are typically selected based on their ability to act as hydrogen bond donors or acceptors, enabling effective modulation of the hydrogen bonding network among water molecules and suppressing water's reactivity. Therefore, WOHEs can maintain the high ionic conductivity characteristic of AEs while simultaneously benefiting from the wide electrochemical stability window typically associated with NAEs (Fig. 1d). Furthermore, in comparison to highly concentrated electrolytes, WOHEs offer reduced preparation complexity and lower costs. In summary, WOHEs demonstrate a more comprehensive set of advantages over other conventional strategies aimed at enhancing the stability of aluminum anodes. However, current research on WOHEs is predominantly based on empirical trial-and-error approaches, with limited and incomplete understanding of their modification mechanisms, electrolyte properties, and unresolved challenges. Hence, in the following section, we aim to systematically summarize and analyze the application and underlying mechanisms of WOHEs in AAMBs, with the goal of providing insights for the future design of high-performance WOHE systems.

2. The Design Principles of WOHEs and Impact on the Evolution of Solvation Structures

The conventional AEs contain a significant amount of free water molecules with high chemical reactivity, resulting in extensive HER and corrosion reactions, ultimately leading to the rapid degradation of the aluminum anode. Additionally, the primary solvation structure of Al^{3+} typically comprises six water molecules.[27,28] This solvation-separated ion pair (SSIP) exhibits relatively high desolvation energy, which constrains the battery's rate performance. By designing WOHEs, the solvation environment of the electrolyte can be effectively modulated. WOHEs can be classified into two categories based on whether additional water is introduced. One category involves mixing specific molar ratios of aluminum hydrate salts with hydrogen bond donors or acceptors (*e.g.*, urea and its derivatives, acetonitrile, *etc.*).[19,26] The coordination between Al^{3+} and the electrolyte components induces a co-crystallization reaction, resulting in a homogeneous liquid mixture at room temperature. The water present in the electrolyte originates entirely from the crystalline water of the metal salts and predominantly exists in the form of bound water rather than free water clusters.[29] This type of electrolyte can be considered a derivative of deep eutectic solvents (DEEs) and is termed hydrated eutectic electrolytes (HEEs) (Fig. 2).[26,30] Such electrolyte systems exhibit high chemical stability due to the predominance of bound water over free water. For example, in the research conducted by Fu *et al.*, the hydrated eutectic electrolyte prepared by mixing $Al(ClO_4)_3·9H_2O$ and methylurea demonstrated an extremely low freezing point of -109.4 ℃, which is significantly lower than that of the conventional $AlCl_3$/[EMIm]Cl IL (-29.8 ℃).[26] Furthermore, the solvation structure of Al^{3+} in this system is distinct. The formation of a loosely bound cluster structure through interactions such as Lewis acid-base interactions, hydrogen bonding, and van der Waals forces between the eutectic components and Al^{3+}.[19] Additionally, the hydration effect of H_2O molecules effectively reduces the viscosity of the electrolyte, thereby lowering the dissociation energy of Al^{3+} than that in ILs or DEEs (Fig. 3).[29]

Another approach involves mixing water with organic solvents in a controlled ratio and subsequently adding aluminum salts to obtain a homogeneous mixture.[15,16,31] By precisely adjusting the proportions of aluminum salts, water, and organic components, the physicochemical properties of the

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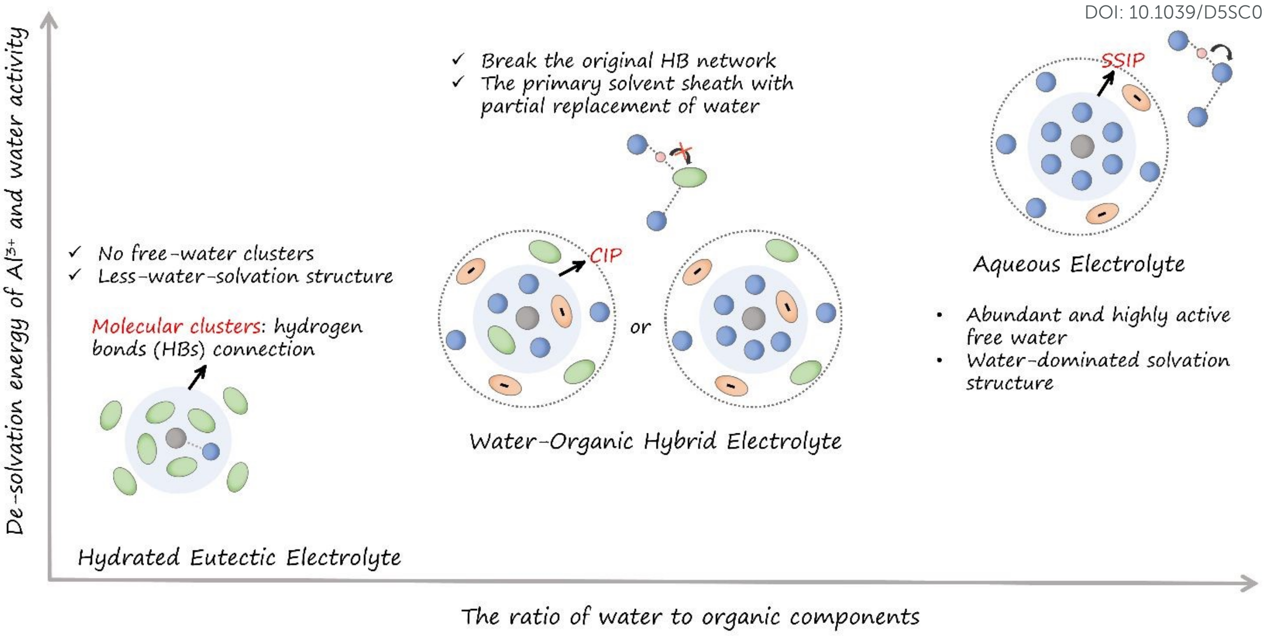

Fig. 3 A schematic illustration depicting the role of WOHEs in modulating the solvation structure and water activity.

electrolyte can be effectively tailored to meet specific performance criteria. This mechanism of electrolyte modification can be attributed to one or both of the following aspects (Fig. 3): (a) The incorporation of polar organic compounds into aqueous electrolytes facilitates the formation of coordination bonds between these compounds and free water molecules, thereby establishing a more robust hydrogen bond interaction network.[15,31] For example, in the multi-component WOHEs composed of $Al(ClO_4)_3·9H_2O$, acetamide, propylene glycol, and water, the organic ligands can serve as competitive hydrogen-bond donors. They disrupt the rigid structure of the water-water hydrogen-bond network, reduce the availability of free water, and weaken the interaction between Al^{3+} and water molecules. Consequently, this WHOE not only substantially reduces the activity of water but also can establish a dynamic equilibrium solvation microenvironment, which offers favorable conditions for the dissociation of Al^{3+}.[32]

(b) Organic compounds can participate in the primary solvation structure of Al^{3+} ions by partially replacing coordinated water molecules. Moreover, when low-conductivity organic components are introduced into the aqueous solvent, the dielectric constant of the solvent system decreases significantly. This may diminish the solvation interaction between Al^{3+} and water, potentially leading to the presence of anions within the primary solvent layer surrounding Al^{3+}. During aluminum deposition, the negatively charged cathode exerts an electrostatic repulsion on the anions, resulting in a significantly lower de-solvation energy barrier for anions compared to that of solvent water, which facilitates the desolvation efficiency of Al^{3+} ions.[24] In the work proposed by Yu. *et al.*, the primary solvation structure of Al^{3+} changes from $[Al(H_2O)_6]^{3+}$ to $[Al(H_2O)_{2.9}(OTf^-)_{1.1}(DMMP)_{0.9}(DMF)]^{1.9+}$, which significantly improves the transport and deposition kinetics performance of Al^{3+}.[17] Furthermore, based on prior studies, in low-concentration aqueous electrolyte systems, hexa-hydrated aluminum ions can function as a Brønsted–Lowry acid, causing the deprotonation of coordinated water by the free water or other hydrogen bond acceptors in the electrolyte.[28,33] Consequently, the decrease in the quantity of water molecules within the solvation shell can effectively mitigating the passivation and hydrogen evolution phenomena on the aluminum anode surface.

Overall, WOHEs mainly regulate the deposition kinetics of Al^{3+} ions and inhibit interface side reactions by designing solvation structures and/or reconstruct the hydrogen bond network. Due to the amphiprotic nature of H_2O, various substances, such as hydrogen bond acceptors and donors, are capable of forming hydrogen-bonded networks with water molecules. This facilitates the immobilization of water molecules and promotes the transformation of the Al^{3+} solvation structure from SSIP to contact ion pairs (CIP) or molecular clusters. Consequently, the design of WOHEs exhibits considerable diversity and warrants further in-depth investigation by researchers.

3. The Influence of WHOEs on the SEI Formation and Interface Chemistry

The WOHEs system comprises multiple components and involves various interactions, including dipole–cation, cation–anion, and dipole–dipole interactions. These interactions not only regulate the phase behavior and solvation structure of the electrolyte but also lead to the formation of unique initial

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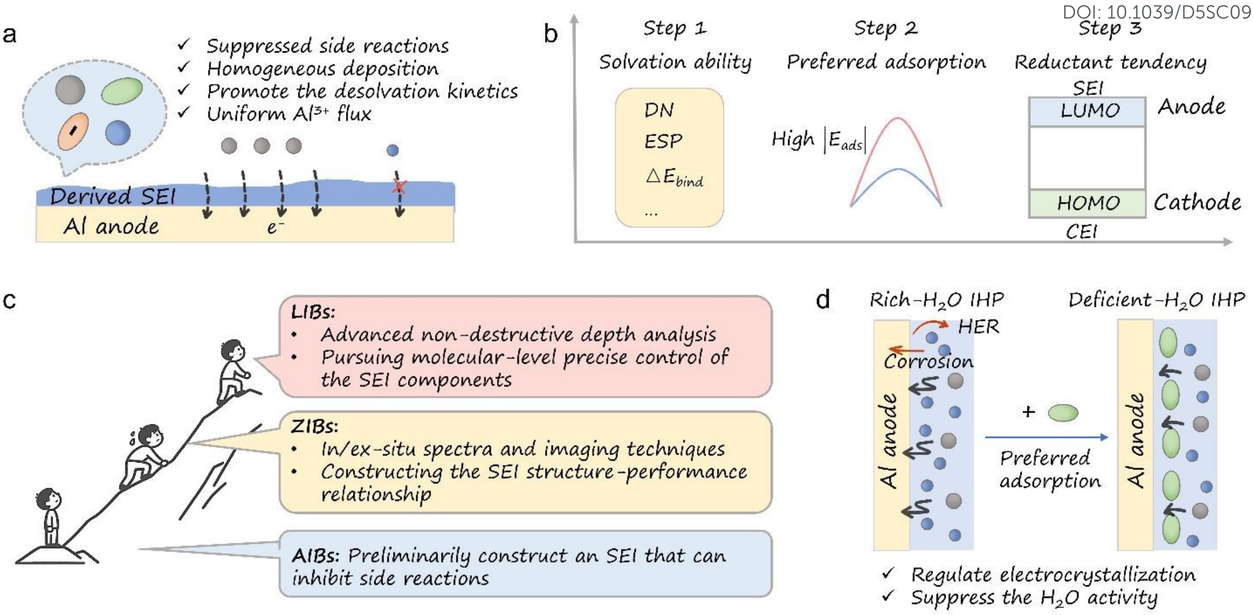

Fig. 4 WOHEs regulating the interface and research progress. (a) The derivatives of SEI formed from WOHEs and their regulatory mechanisms governing aluminum deposition interface behavior. (b) A strategy for the pre-selection of organic ligands based on theoretical simulations to guide SEI evolution. (c) Research advances in the characteristics and underlying mechanisms of SEI in lithium-ion, zinc-ion, and aluminum-ion batteries. (d) Schematic illustration of the mechanism by which aluminum deposition behavior is optimized through modulation of the EDL structure without direct participation in SEI formation.

adsorption configuration within the inner Helmholtz plane (IHP) on the aluminum surface prior to charge transfer. As the anode surface undergoes progressive polarization, solvent molecules, anions, and organic ligands within the IHP decompose at distinct reduction potentials, with their reduction products forming an in-situ SEI.[30] Consequently, the chemical composition of the electrolyte and the distribution of species within the electric double layer (EDL) at the EEI play a decisive role in determining the composition and architecture of the SEI. Drawing upon studies in lithium-ion and zinc-ion batteries, the SEI typically exhibits a bilayer structure: the inner layer predominantly consists of inorganic compounds formed through the complete reduction of solvents, which provides high mechanical strength and effectively suppresses dendrite growth while protecting the metal anode from electrolyte corrosion; the outer layer is primarily composed of irreversibly or partially reduced organic species, exhibiting a porous morphology that facilitates electrolyte infiltration and promotes ion desolvation.[34-36] The chemical and structural properties of the SEI directly influence the cycling stability of the metal anode and the electrochemical performance of the full cell. For instance, Zhang *et al.* performed XPS analysis and found that, the cycled Al anode surface developed an SEI containing organic components (-CF_3) and inorganic species (*e.g.*, $AlPO_4$) in a mixed electrolyte composed of glycerol, sodium beta-glycerophosphate pentahydrate, H_2O, and $Al(OTf)_3$.[16] The resulting interface effectively suppresses water-induced side reactions, thereby enabling the Al||Al symmetric cell to achieve a cycling stability of up to 1,000 h at a current density of 0.05 mA cm^{-2}. Furthermore, the symmetric cell maintains stable operation for over 500 h at -20 °C and 1,000 h at 60°C under extreme temperature conditions. A stable SEI not only effectively protects the aluminum electrode against corrosion and passivation, but also regulates the distribution of Al^{3+} flux at the EEI and modulates ion transport behavior within the SEI layer, thereby facilitating uniform aluminum plating and stripping (Fig. 4a). In the study by Chen *et al.*, methyl carbamate (MC) was systematically investigated as a co-solvent.[24] MC exhibited preferential adsorption on the aluminum surface, with a lowest unoccupied molecular orbital (LUMO) energy level of 0.528 eV lower than that of other ligands and electrolyte components, indicating higher electron affinity. Consequently, MC is thermodynamically favored to undergo reduction and participate in SEI formation. Quantitative analysis via electrochemical impedance spectroscopy (EIS) demonstrated that the MC-containing SEI possesses excellent ionic conductivity, with a significantly reduced activation energy for Al^{3+} migration. This suggests that the SEI enhances desolvation kinetics during aluminum deposition, promoting homogeneous Al^{3+} flux and yielding a smooth deposition morphology.

Based on a comprehensive understanding of the film-forming mechanism, the structure of the SEI can be precisely regulated through rational design of the components in WOHEs. For example, density functional theory (DFT) calculations based on key parameters such as donor number (DN), electrostatic potential (ESP), and binding energy can be employed to predict

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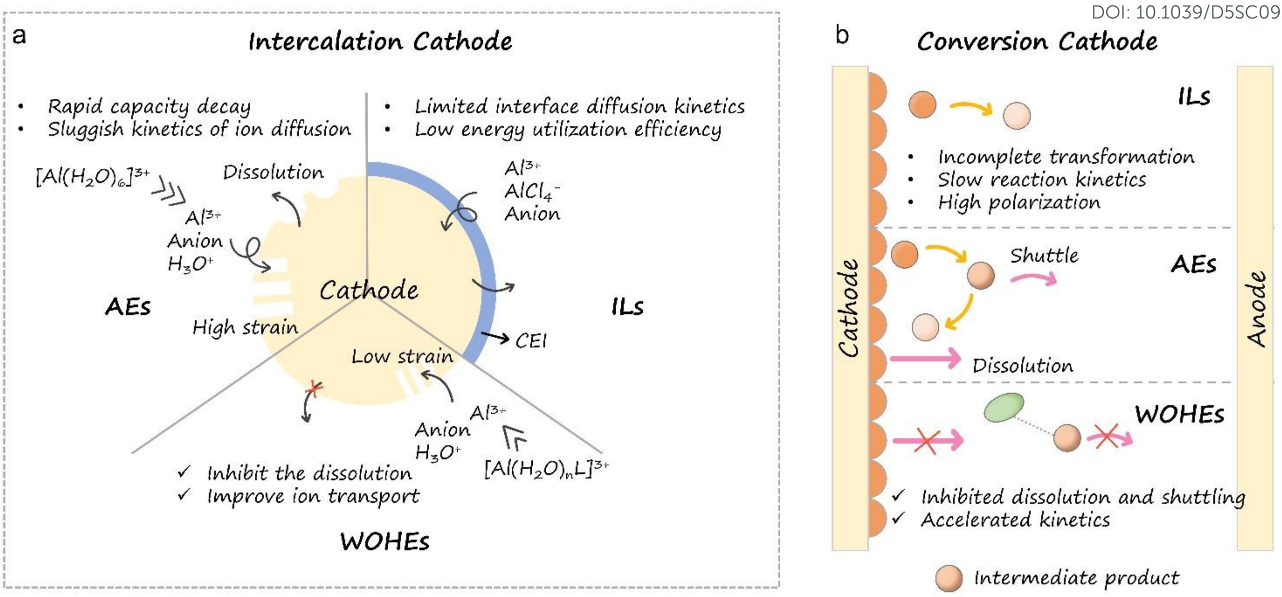

Fig. 5 A schematic illustration depicting the comparative analysis of the advantages and challenges of (a) intercalation cathodes and (b) conversion cathodes across various electrolyte systems.

the propensity and effectiveness of organic ligands in modulating the solvation structure of aluminum ions. Furthermore, by evaluating the adsorption energies of organic molecules on the aluminum electrode surface, candidate molecules exhibiting favorable adsorption behavior can be identified. In conjunction with molecular orbital theory, the reactivity of these molecules in interfacial electron transfer processes may also be assessed, thereby offering theoretical guidance for tailoring the chemical composition and functional properties of the SEI, enabling structured assembly and precise performance control (Fig. 4b). It should be emphasized that, although the SEI plays a pivotal role in determining the overall performance of AIBs, current knowledge regarding its formation mechanisms, interfacial physicochemical characteristics, and influence on electrode reaction kinetics and electrochemical stability remains significantly less systematic and thorough compared to that in lithium-ion or zinc-ion battery systems. Therefore, to advance the practical deployment of AAMBs, it is imperative to conduct more in-depth mechanistic studies and systematic investigations into fundamental interfacial reaction theories, in situ characterization techniques, and multi-scale simulation approaches (Fig. 4c).

Furthermore, the components in WOHEs may not participant in forming SEI due to their high LUMO levels, instead, they can regulate Al deposition behavior through preffered adsorption, thereby modifying the distribution of species within the Helmholtz layer (Fig. 4d). For example, studies have shown that in the specifically designed ternary hydrate eutectic electrolyte composed of aluminum nitrate hydrate, manganese nitrate hydrate, and N,N-dimethylacetamide, DMA molecules exhibit a higher adsorption tendency on the Al anode surface compared to water molecules.[29] This preferential adsorption not only significantly suppresses the HER at the electrode/electrolyte interface, but also results in a substantial overlap between the electron density of the N atom in the DMA molecule and that of the Al atom. This electron density overlap suggests that electron transfer is facilitated when DMA adsorbs onto the Al surface, thereby modulating the kinetics of the electrocrystallization process.

4. The Significant Potential Exhibited by WOHEs in Enhancing the Performance of Cathode Materials

The cathode material is one of the key factors that significantly influence the performance of AAMBs. Currently, commonly used cathode materials in AAMBs mainly include transition metal oxides,[14,37-39] Prussian blue analogues,[40,41] carbon-based materials,[42,43] and organic compounds.[44,45] With continuous advancements in the development and structural design of various cathode materials, multiple energy storage mechanisms, such as intercalation/deintercalation, conversion reactions, and redox reactions involving organic functional groups have been extensively investigated. However, the current electrochemical performance of most commonly used intercalation-type cathode materials in AAMBs remains unsatisfactory. This is primarily attributed to sluggish interfacial charge transfer kinetics resulting from the strong interaction between Al^{3+} and water molecules. More critically, the high charge density of Al^{3+} induces a pronounced polarization effect during the intercalation/extraction processes within the cathode, leading

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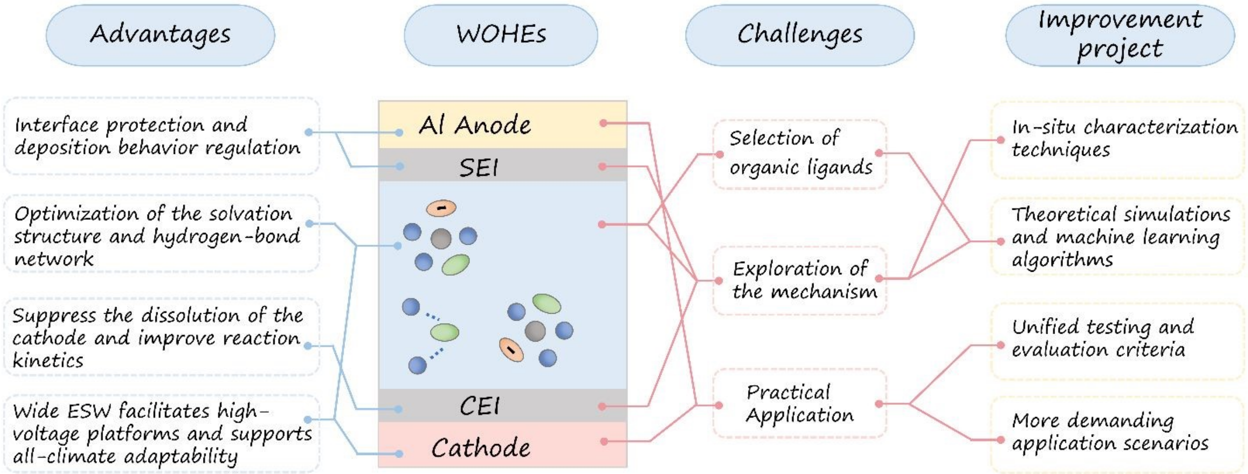

Fig. 6 Schematic diagram illustrating the mechanism of WOHBs on AMMBs and ultimate goals for future research and applications.

to lattice distortion and irreversible dissolution, which contribute to rapid capacity decay in AAMBs (Fig. 5a).[20,45] In non-aqueous electrolyte systems, particularly those employing common ILs, although aluminum-based batteries exhibit excellent cycling stability and Coulombic efficiency (CE) approaching 100%, the active species inserted into the host material are $AlCl_4^-$ group rather than Al^{3+} (or with H_3O^+). This fundamental difference results in a significantly lower practical mass energy density compared to theoretical expectations.[46] Furthermore, the robust electrostatic interaction between the cations and anions in the ILs elevates its viscosity, leading to suboptimal wettability of the porous electrode and a slower rate of ion transport.[47] On the contrary, in WOHEs, as previously noted, the decrease in the coordination number of water molecules in the Al^{3+} solvation shell facilitates the formation of a low-coordination solvation structure. This structural optimization effect offers several advantages. Firstly, it can notably enhance the insertion/extraction kinetics of Al^{3+} within the electrode. The volume strain alleviation effect can substantially improve the long-cycle stability of the cathode.[48] Secondly, it can expedite the transport kinetics of Al^{3+} in the host, thus effectively reducing the voltage polarization of the battery and enhancing the overall energy efficiency of the battery. Furthermore, owing to the effective inhibition of HER, the full cell can maintain relative stability within a broader voltage range.[25]

Additionally, in non-aqueous electrolyte systems, it has been verified that organic ligands or electrolyte anions can undergo selective decomposition on the cathode surface, thereby forming a stable cathode-electrolyte interface (CEI).[49] This interface layer can effectively prevent the continuous corrosion of the electrode by electrolyte components. This research finding provides significant references for the interface regulation research of the WOHEs. Nevertheless, the specific evolution pathways and influence mechanisms of each component in the WOHE for the CEI, remain unclear. These are crucial scientific issues that urgently require in-depth exploration in this field.

In addition to intercalation electrodes, conversion-type cathodes such as I_2, Br_2, and S have garnered significant attention in AIBs.[46,50-52] Taking the I_2 cathode as an example,[50] in less electrochemically active non-aqueous electrolytes, such as ILs, high current densities can readily increase internal resistance and induce substantial polarization. This often leads to the direct reduction of I_2 to I^-, bypassing the formation of intermediate species such as I_5^- and I_3^-, resulting in reduced specific capacity and a lower discharge plateau compared to AEs. Additionally, it is often accompanied by severe side reactions and the generation of Cl_2 gas.[53] Although conversion cathodes exhibit faster reaction kinetics in the application of AEs, its intermediate products possess a relatively high solubility and are liable to experience inter-electrode migration. This uncontrolled shuttle behavior not only results in the irreversible loss of active materials but also substantially reduces the CE of the battery.[54] To tackle these issues, Yu and his team proposed a cost-effective hydrated molten electrolyte system composed of $AlCl_3{\cdot}6H_2O$ and organic halide salts.[52] The introduced $PY14^+$ organic cation can electrostatically interact with polyhalide species (*e.g.*, Br_{2n+1}^- and $BrCl_2^-$) to form a water-insoluble phase, thereby inhibiting their dissolution to the aqueous electrolyte. Meanwhile, the halide anions (Br^-/Cl^-) reside in the outer solvation shell of the cation, where weak coordination facilitates rapid dissociation and enables efficient surface charge transfer during the bromine conversion process. Furthermore, more than 98% of the water molecules in the electrolyte participate in the formation of tightly bound ionic solvation structures, effectively suppressing water activity. Owing to these advantageous features, the assembled Al||Br battery achieved a high energy density of 276 Wh L^{-1}, comparable to that of commercial lithium-ion batteries. Thus,

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the WOHEs exhibit significant potential for practical applications in mitigating the dissolution and shuttling of conversion electrodes and improving reaction kinetics (Fig. 5b).

5. Summary and Prospects

Due to the low cost, environmental friendliness, high theoretical specific capacity, and abundant reserves of aluminum, AAMBs have demonstrated significant potential for large-scale energy storage applications. In this perspective, we outline the primary challenges associated with AAMBs, with particular focus on the fundamental mechanisms of WOHBs in such systems. These mechanisms mainly involve the reconfiguration of the solvation environment, regulation of interfacial behavior, induction of special SEI formation, and the application prospects in enhancing the performance of the cathode. Compared to WIS or deep eutectic electrolytes, WOHBs offer advantages such as higher ionic conductivity, lower viscosity, and reduced cost, suggesting that WOHBs are a promising system for developing high-performance and environmentally sustainable AAMBs.

Although considerable progress has been made in improving AAMBs' performance using WOHBs, several critical issues and future research directions warrant further investigation: First, while the incorporation of organic components can effectively optimize the solvation environment of Al^{3+} ions, it may also influence the ionic conductivity and viscosity of the electrolyte. This phenomenon can be attributed to changes in the size of the Al^{3+} solvation shell or strong interactions with water molecules. Therefore, achieving a balance between the beneficial properties of both eutectic and AEs remains a key challenge. Additionally, in multi-component WOHBs systems, the interactions among individual components and their synergistic effects on electrode performance merit in-depth exploration.

Secondly, although certain electrolytes containing multiple organic components have considerably improved the stability of aluminum anodes, the selection of individual constituents and the optimization of their proportions are predominantly determined through empirical approaches. This significantly elevates operational costs and highlights the need to integrate artificial simulation or theoretical calculations to predict the compatibility and effectiveness of each organic component in advance. Such predictions can be based on relevant physicochemical parameters, including Lewis acidity and basicity, dielectric constant, Gutmann donor number, dipole moment, electrostatic potential, and the ability to form stable and uniform SEI or CEI. Furthermore, the range of water-soluble aluminum salts capable of forming stable low-melting liquid electrolytes remains limited. For instance, only $Al(ClO_4)_3{\cdot}9H_2O$, a halogen-rich aluminum salt, is currently capable of forming such stable low-melting solutions when combined with specific hydrogen bond donors. Future research could leverage human-computer collaboration to develop WOHEs with enhanced performance and reduced costs.

Thirdly, the chemistry of the EEI and the dynamics of ion/charge transport are two critical factors governing the overall performance of batteries. Consequently, understanding how WOHEs modulate the electrochemical behavior at the EEI and influence the evolution of the SEI/CEI has become a central scientific challenge that warrants thorough investigation. To systematically elucidate this mechanism, future research should integrate a suite of advanced characterization techniques and computational simulations. On one hand, non-destructive analytical methods, such as infrared spectra, solid-state nuclear magnetic resonance, and energy-dispersive X-ray spectra, can enable detailed characterization of the nanoscale structure and chemical composition of the SEI/CEI. On the other hand, first-principles calculations, molecular dynamics simulations, augmented by machine learning algorithms, can be employed to establish a structure-activity relationship between the physicochemical properties of the SEI/CEI and electrochemical kinetic parameters, thereby facilitating a multiscale understanding and precise prediction of interfacial processes.

Fourth, the innovative modulation of the electrolyte solvation structure through WOHEs enables a significant expansion of its application potential, extending from the anode interface to the cathode interface. By substantially widening the ESW of the electrolyte, WOHEs effectively suppress the water decomposition reaction at elevated potentials, thereby enabling the integration of high-voltage cathode materials that were previously incompatible with aqueous systems due to thermodynamic instability. Consequently, the design and development of novel high-capacity, high-voltage cathode materials compatible with WOHEs will be crucial to achieving high energy density and rapid charging performance in AIBs.

Finally, since WOHBs have the potential to reconfigure the hydrogen bond network and solvation environment within the system, they may alter the freezing and melting points of the electrolyte. Consequently, the performance of these electrolytes across a wide temperature range should become a key focus of future research. Moreover, most current studies on aqueous aluminum-ion batteries are conducted using coin cells, where the applied current density and capacity density are typically very low (<1 mA cm^{-2} @ 1 mAh cm^{-2}). Under such conditions, it may be difficult to accurately assess the practical application potential of AAMBs in larger or more realistic energy storage systems. Therefore, more rigorous and comprehensive testing and evaluation methods, such as investigations into depth of discharge, low N/P ratio (negative electrode capacity/positive electrode capacity), and low E/C ratio (electrolyte volume/capacity), should be implemented to better reflect real-world performance.

Author contributions

L.L. collected and organized the data. L.L. and Y.H. co-wrote the paper. Y.H. and H.W. supervised this work.

Conflicts of interest

The authors declare no conflicts of interest.

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