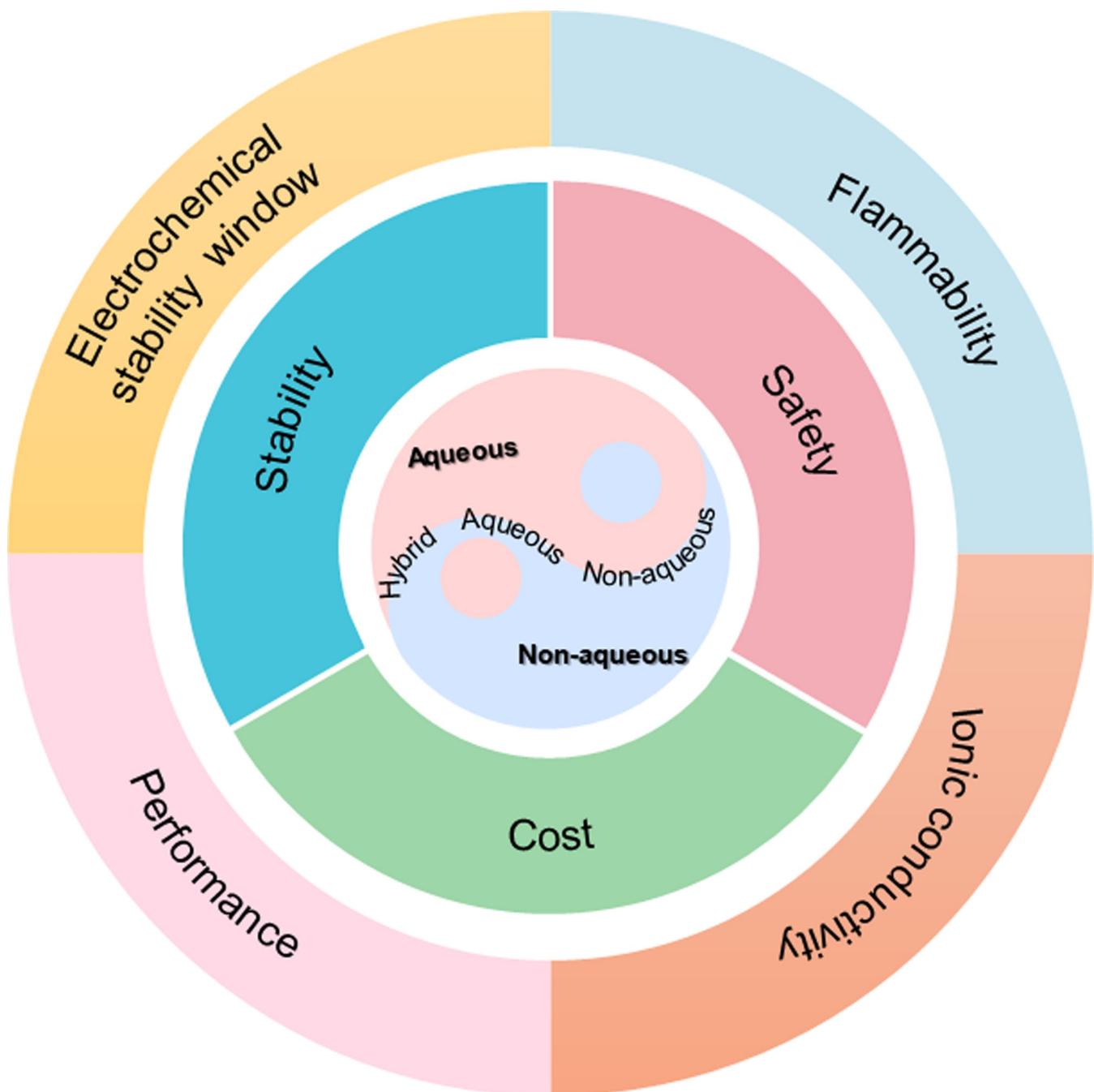


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Hybrid Aqueous/Non-aqueous Electrolytes for Lithium-Ion and Zinc-Ion Batteries: A Mini-Review

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In recent years, the development of aqueous lithium-ion batteries and aqueous zinc-ion batteries has received extensive attention thanks to the advantages of high safety, environmental friendliness, and easy assembly conditions. However, aqueous batteries are always restricted in terms of limited cycling stability and low energy density due to their intrinsically narrow electrochemical window, hydrogen evolution, and side reactions. These problems can be remarkably alleviated by

hybridizing aqueous/non-aqueous electrolytes; however, few detailed discussions on relevant strategies have been reported. In this mini-review, we summarize the latest progress and contributions of various hybrid aqueous/non-aqueous electrolytes for rechargeable aqueous lithium-ion batteries and aqueous zinc-ion batteries. The current challenges and development directions are also discussed for hybrid electrolytes.

1. Introduction

After years of commercial development, lithium-ion batteries have been widely used in portable electronic devices, electric vehicles, and stationary storage for various renewable energy due to their high energy density and long life.^[1] Nevertheless, conventional lithium-ion batteries use organic solvents in electrolytes, which not only raises the requirements for a strictly dry manufacturing environment but also poses challenges to large-scale applications due to their flammability and possible toxicity.^[2] For safety reasons, there has been strong interest in replacing the highly flammable non-aqueous solvents with intrinsically non-flammable solvents, such as H₂O.^[3] H₂O solvent provides advantages such as high ionic conductivity, low cost, and non-flammability, but shows a narrow electrochemical stability window (ESW) of only 1.23 V.^[4] In traditional dilute salt-in-water aqueous electrolytes, the ESW could be about 2.0 V dynamically,^[5] which still restricts the applications in high-energy batteries (Figure 1a). Moreover, H₂O could deteriorate the chemical and structural stability of electrode materials in aqueous rechargeable batteries, resulting in unsatisfactory electrochemical performance.^[6] To reduce H₂O activity and extend the ESW of aqueous electrolytes, various water-in-salt-type electrolytes (WiSEs) and hydrate melts have been proposed, in which the salt exceeds the solvent in both weight and volume.^[7] Accordingly, WiSEs enable many electrode materials to operate stably in aqueous lithium-ion batteries (ALIBs) and resolve the low Coulombic efficiency (CE) and dendrite growth of zinc in aqueous zinc-ion batteries (AZIBs).^[8] However, their applications are impeded by their high viscosity, high cost, and strong corrosivity from the extremely high concentration of salts.^[9]

Recently, researchers turned their attention to hybrid aqueous/non-aqueous electrolytes. The addition of functional organic species to WiSEs is widely studied to further tune the charge transport and electrochemical stability of aqueous electrolytes, which exhibits various merits. First, hybrid aque-

ous/non-aqueous electrolytes could regulate the viscosity and ionic conductivity, which are of significant importance to the rate performance of devices. Second, organic species with a high donor number could enter the first solvation shell, thereby adjusting the local Li⁺-coordinating environment and reducing H₂O activity. Meanwhile, the additional organic species potentially fill the inner Helmholtz plane due to the preference adherence to the anode surface and thereby pushing H₂O away from the electrode interface, leading to improved interfacial stability in aqueous batteries.^[10] Third, strong corrosivity towards current collectors, tabs, and packaging materials by concentrated amide-based salts would be greatly retarded in the hybrid aqueous/non-aqueous electrolytes. Forth, hybrid aqueous/non-aqueous electrolytes could significantly reduce the cost of WiSEs, which is essential for practical applications.

In this mini-review, we comprehensively discuss the latest progress of hybrid aqueous/non-aqueous electrolytes in ALIBs and AZIBs, highlighting their unique electrochemistry and how the hybrid solvation structures adjust the electrochemical stability of rechargeable aqueous batteries. We also present further perspectives on designing aqueous hybrid electrolytes for aqueous energy storage devices.

2. Hybrid Aqueous/Non-aqueous Electrolytes

Fundamentally, the hybridization of organic species and aqueous electrolytes could adjust the solvation structures due to competing interactions between H₂O and organic species towards the cations and anions.^[11] In this section, hybrid aqueous/non-aqueous electrolytes with different types of organic species are reviewed, including small organic molecules, molecular crowding agents, ionic liquids, deep eutectic solvents, and polymers (gels).

2.1. H₂O-small organic molecules hybrid electrolytes

Small polar organic molecules used in batteries are typically miscible with aqueous electrolytes, which can tune the solution chemistry and electrochemistry of aqueous electrolytes. The localized solvation structure and hydrogen bonding network of aqueous electrolytes could be remarkably adjusted based on the properties of added small organic molecules. Different types of small organic molecules are discussed in the following parts.

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2.1.1. Solvating co-solvents

The Li⁺ ions are typically solvated by the organic polar solvents in non-aqueous electrolytes.^[12] Certain small polar organic solvents can replace partial H₂O in the first coordination sheath of Li⁺ in the aqueous electrolyte, thus stabilizing the interface in aqueous electrolytes.^[10,13] Wang et al. first demonstrated a hybrid electrolyte in ALIBs with the introduction of dimethyl carbonate (DMC) into a concentrated LiTFSI aqueous solution, at an apparent LiTFSI concentration of ~14 m.^[14] It was reported that DMC molecules participated in the coordination with Li⁺ through both carbonyl oxygen and ethereal oxygen, resulting in two Li⁺ solvates bridged by DMC to form the Li⁺₂(DMC) (Figure 2a). The negative side voltage of 14 m LiTFSI/DMC-H₂O electrolyte thus was extended to 1.0 V compared with 1.9 V in 21 m LiTFSI electrolytes. Furthermore, the Li⁺₂(DMC) accordingly cooperated with the Li⁺(TFSI)₂ to generate insoluble Li₂CO₃-LiF solid electrolyte interface (SEI) layers by sequence on the surface of anodes (Figure 2b). The SEI layer contained organic alkyl carbonate species from DMC molecules, which further helped to screen H₂O from the electrode surface and assist in de-solvating Li⁺ from H₂O and diffusing Li⁺ toward the anode. The addition of DMC into Zn²⁺-based electrolytes also promoted smooth and stable interfacial reactions for Zn anodes in AZIBs.^[15]

Besides carbonates, introducing ether solvents such as tetraethylene glycol dimethyl ether (TEGDME),^[13b] 1,2-dimethoxyethane (DME),^[16] and triglyme^[17] into aqueous electrolytes were also reported. For instance, TEGDME in 15 m LiTFSI/TEGDME-H₂O aqueous electrolyte could kinetically extend the ESW to 4.2 V, thus realizing a 2.5 V Li₄Ti₅O₁₂||LiMn₂O₄ full battery with an excellent energy density of 120 Wh kg⁻¹ for 500 cycles. The added ether-based co-solvents could decrease the hydrogen evolution reaction (HER) in the electrolytes by coordinating with metal ions to reduce the number of coordinated H₂O.

However, the moderate viscosity of carbonate and ether-based electrolytes still showed limitations for low-temperature

applications. Designing hybrid aqueous electrolytes with high ionic conductivity, low viscosity, and extremely low freezing point is important for the low-temperature performance of aqueous batteries. Different types of salt can change the mutual interaction among dissociated cations, anions, and H₂O.^[18] For example, ZnCl₂,^[19] LiNO₃,^[20] and LiCl^[21] could lower the freezing point of aqueous electrolytes. In addition, employing salts with high dissociation ability,^[22] adding low viscosity and low-freezing point co-solvents^[23] could be beneficial to enhance the low-temperature performance of rechargeable batteries. Acetonitrile (AN) with low freezing points, was typically selected to optimize low-temperature performance and enhance the reaction kinetics in aqueous and non-aqueous batteries.^[24] Xu et al. reported that the AN-based hybrid aqueous lithium-ion electrolyte (1LiTFSI-1.11AN-1.11H₂O) exhibited a wide liquid range down to -60 °C. Unfortunately, such electrolyte could only enable the Li₄Ti₅O₁₂||LiMn₂O₄ cells to cycle at 0 °C and showed rapid performance degradation as temperature decreased to -20 °C.^[13a] Besides these macro properties of electrolytes such as viscosity, the microstructures of Li⁺ solvation and de-solvation process are more correlated to the low-temperature performance.^[25] Strong bonding interaction between the organic solvent and Li⁺ causes sluggish interfacial ion transport of Li⁺ at the electrode interface, which is considered as one of the major factors that limit the low-temperature performance of aqueous electrolytes.^[26] Introducing organic solvents with moderate binding energy to Li⁺ could be helpful to enable appropriate reaction kinetics at low temperatures. Xing et al. reported LiTFSI/DOL-H₂O hybrid electrolytes with weak binding strength for Li⁺-DOL solvation complex.^[13c] This electrolyte enabled an excellent electrochemical performance for the Li₄Ti₅O₁₂||LiMn₂O₄ ALIBs at -20 °C and remained normal operational at even -50 °C. The excellent low-temperature performance originated from the lower solvation energy, which enabled the fast Li⁺ de-solvation process at low temperatures.

Besides, highly polar solvating co-solvents have also been studied for aqueous electrolytes for AZIBs.^[15,27,33] For example,



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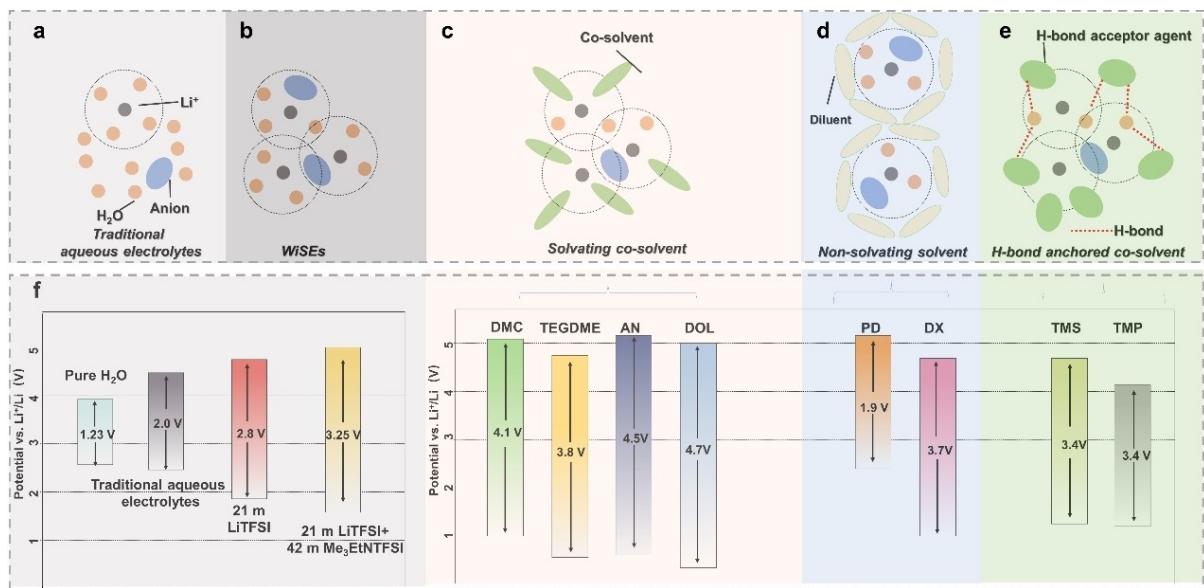


Figure 1. a, b) Solvation structures of cations in traditional dilute aqueous electrolyte and WiSEs. c–e) Hybrid aqueous electrolytes with different small organic co-solvents: c) solvating organic solvent, d) non-solvating dilute solvent, e) H-bond anchored solvent. f) Electrochemical stability window of different hybrid aqueous electrolytes corresponding to representative solvation structures. The data in Figure 1(f) are from Refs. [4,5,7a,k,10,13a–c,37,29,30,42].

strongly polar dimethyl sulfoxide (DMSO) was employed to preferentially solvated with Zn²⁺ and excluded H₂O from the solvation sheath of Zn²⁺ to promote the smooth Zn deposition and improve electrochemical performance (Figure 2c).^[27] AN is another commonly used co-solvent to regulate the solvation structure of Zn²⁺ and exclude partial H₂O molecules from the inner coordination sheath of Zn²⁺ via the strong solvation strength between Zn²⁺ and AN molecules.^[28,34] Zhang et al. demonstrated that in the optimized electrolyte of 1 m ZnSO₄/90% H₂O-10% AN, AN molecule could replace up to three H₂O molecules in the Zn(H₂O)₆²⁺ complex (Figure 2d), showing a high CE of 99.64% on average up to 1000 cycles with homogeneous nucleation and smooth growth of Zn. It notes that divalent Zn²⁺ might suffer from stronger electrostatic interaction with solvents compared with monovalent Li⁺.^[35] Strong solvation strength results in large energy barrier for desolvation and thus sluggish reaction kinetics for aqueous Zn batteries. It would be important to balance electrochemical stability and appropriate reaction kinetics of aqueous electrolytes in practical use.

2.1.2. Non-solvating/sparingly solvating diluents

Unlike the solvent-dominated interfacial chemistry formed by coordinating co-solvent, diluted highly concentrated electrolytes with non-solvating/sparingly solvating solvents have been recently widely investigated in non-aqueous localized high-concentration electrolytes (LHCEs).^[36] But it is still rare to develop diluted WiSEs with non-solvating/sparingly solvating co-solvents due to the typical immiscibility of such low-solvation solvents in aqueous electrolytes. LHCEs present reduced overall salt concentration, but retain the solvation

structure of contact ion pairs and ion aggregates in highly concentrated electrolytes.^[11] Therefore, it is believed that LHCEs could provide possible solutions to address the issues of high salt concentration, such as poor wettability, high viscosity, and high cost.

Recently, Wang et al. reported an aqueous LHCE electrolyte by using cheap inorganic LiNO₃ as salt and 1,5-pentanediol (PD) as a diluent in aqueous electrolytes, which exhibited an extended ESW of 2.9 V vs. Li/Li⁺.^[37] Compared to the pure H₂O and 12.5 m LiNO₃ in H₂O electrolyte, the HER onset potential of the LHCE electrolyte (12.5 m LiNO₃ in H₂O:PD) was broadened to a more negative potential (2.27 V vs. Li/Li⁺). However, the redox potential of the Mo₆S₈ anode was still lower than the HER onset potential of the LHCE, which would trigger H₂O decomposition during the battery cycling and thus reduce the battery reversibility. This may be attributed to the absence of highly electronically insulating LiF derived from LiTFSI in the SEI layer, which has been widely evidenced in ALIBs.^[7a,e,38] Ren et al. employed the non-polar 1,4-dioxane (DX) solvent as an over-crowding agent to generate an “overcrowded” electrolyte with intensified ion-solvent interactions in the inner solvation structure of Li⁺ in 1.9 m LiTFSI/DX-H₂O electrolyte (Figure 2e).^[29] This overcrowded water-ion solvation structure favored the formation of a robust LiF-enriched SEI, which extended the cathodic window to 1.0 V at a low salt concentration of 1.9 m. Li₄Ti₅O₁₂ | LiMn₂O₄ full cells with the 1.9 m LiTFSI/DX-H₂O hybrid aqueous electrolytes demonstrated stable cycling over 200 cycles at 0.57 C with a capacity retention of 88.5%. Though few works have been reported for aqueous LHCEs, the introduction of non-solvating or sparingly solvating solvents provides an alternative approach to adjusting the local and nearby solvation structure of cations with enhanced electrochemical stability. A deep understanding of the interactions of

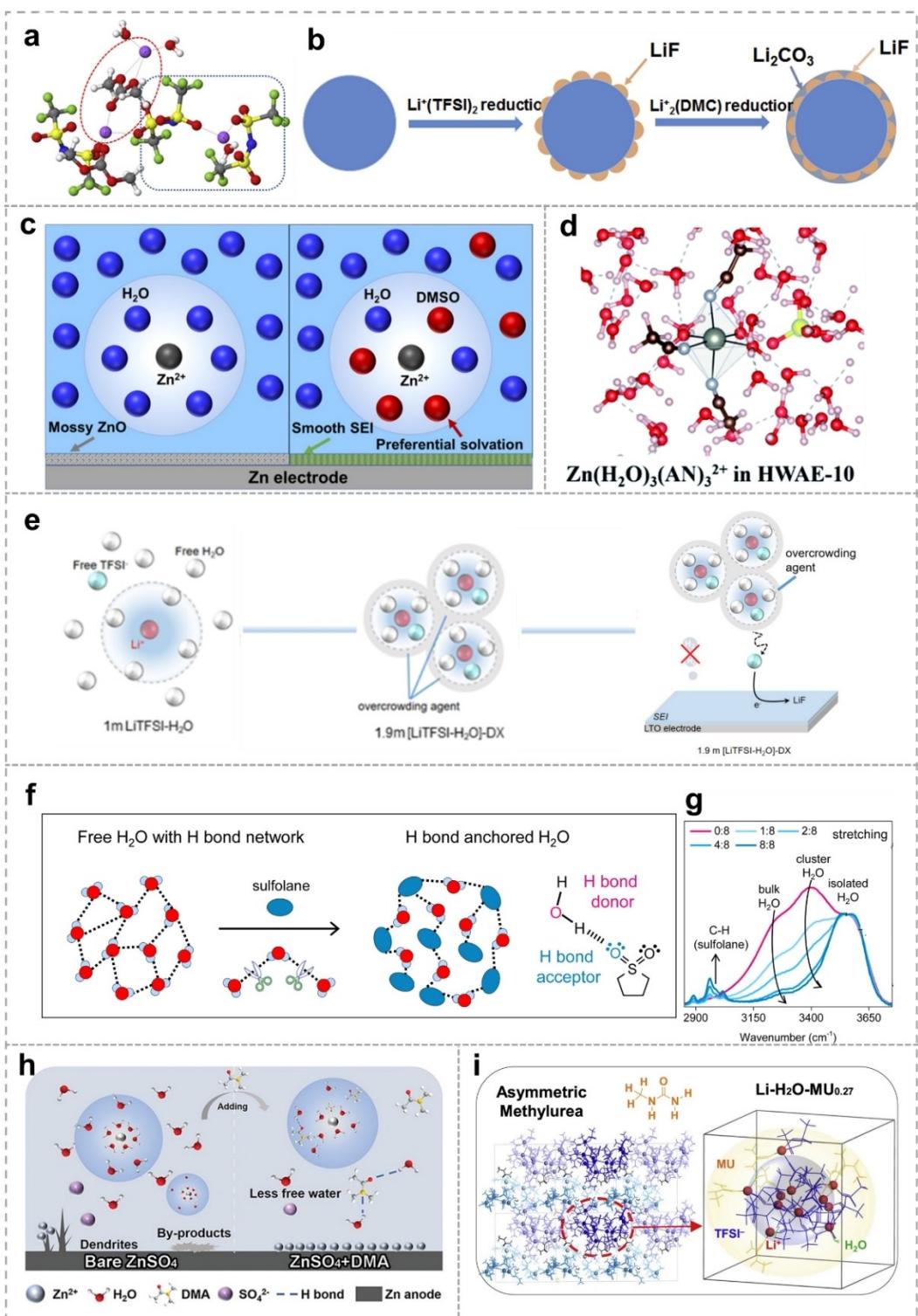


Figure 2. a) Representative liquid structure for the 14 m LiTFSI/DMC-H₂O electrolyte. b) Schematic illustration of the anode SEI formation in LiTFSI/DMC-H₂O hybrid electrolytes. Reproduced with permission from Ref. [14]. Copyright (2018) Elsevier. c) Scheme of Zn²⁺ solvation structure and zinc surface passivation in H₂O (left) and H₂O-DMSO (right) solvents. Reproduced with permission from Ref. [27]. Copyright (2020) American Chemical Society. d) Snapshots of the simulations of the 1 m ZnSO₄/90%H₂O-10%AN (HWAE-10) electrolyte. Reproduced with permission from Ref. [28]. Copyright (2020) The Royal Society of Chemistry. e) Schematic illustration of the anode SEI formation in DX-H₂O hybrid electrolytes. Reproduced with permission from Ref. [29]. Copyright (2021) American Chemical Society. f) Schematic illustration of intermolecular interactions of H₂O-hydrogen bond-anchored electrolytes. g) The stretching region of normalized FTIR spectra of LiTFSI/TMS-H₂O electrolytes. Reproduced with permission from Ref. [30]. Copyright (2022) Elsevier. h) Schematic illustration of the solution structures and interface reactions in ZnSO₄ (left) and ZnSO₄/DMA-H₂O (right) hybrid electrolytes. Reproduced with permission from Ref. [31]. Copyright (2022) Wiley-VCH. i) Solution structures of Li-H₂O-MU_{0.27} solution over a larger length scale (left). The Li-H₂O-MU_{0.27} solution contains various nanoscale clusters with core-shell-like solvation structures (right). Reproduced with permission from Ref. [32]. Copyright (2022) Elsevier.

the diluents in aqueous electrolytes and the cation transport properties in such electrolytes could be important to design future high-performance aqueous electrolytes for practical use.

2.1.3. H-bond anchored co-solvents

Besides the regulation of the inner solvation of cations such as Li^+ and Zn^{2+} , tuning the hydrogen-bonding interactions with H_2O molecules is another approach to adjusting electrochemistry properties in aqueous electrolytes.^[39] Free H_2O in aqueous electrolytes are the H_2O molecules that interact with each other through the H-bonded ($\text{H}-\text{O}\cdots\text{H}$) network. Disruption of the $\text{H}_2\text{O}-\text{H}_2\text{O}$ H-bonds by introducing new strong H-bonds would restrict the activity of H_2O from the perspective of thermodynamics.^[40] Sulfolane (TMS) molecule possesses two pairs of lone electrons on each oxygen atom and could significantly break the original H-bond network and build a new reinforced H-bond network, which confines the activity of H_2O by modulating H-bonds. Recently, TMS was introduced as a H-bond anchored co-solvent into aqueous electrolytes to enhance the electrochemical stability of rechargeable aqueous batteries (Figure 2f and g).^[30] TMS also showed the advantages of miscibility with H_2O and low cost, which favored the application of such electrolytes.^[39] An aqueous $\text{Li}_4\text{Ti}_5\text{O}_{12} \parallel \text{LiMn}_2\text{O}_4$ full cell with the H-bond anchored electrolyte (LiTFSI/TMS- H_2O) achieved a high energy density of 141 Wh kg^{-1} and stable cycling over 1000 cycles at 5°C and high Coulombic efficiency of 99.5%–99.9%.^[30] TMS was also employed as the strong H-bond anchored co-solvent in 3 m $\text{Zn}(\text{TfO})_2$ aqueous electrolytes for aqueous zinc-ion batteries. Without entering the inner coordination sheath of Zn^{2+} , TMS was dominantly located in the second coordination shell and significantly strengthened the H-bond network through stronger interactions among H_2O , TfO^- and TMS. $\text{Zn} \parallel \text{V}_2\text{O}_5$ full cells with the 3 m $\text{Zn}(\text{TfO})_2/\text{TMS-}\text{H}_2\text{O}$ hybrid aqueous electrolytes delivered excellent cycling stability over 20000 cycles with 85% capacity retention.^[41]

Very recently, trimethylphosphate (TMP) was reported to exhibit similar enhancement for the H-bond network in aqueous electrolytes.^[42] Besides, the TMP- H_2O interactions contributed to the formation of stable SEI layers composed of phosphate and LiF salts for the extended ESW to 3.7 V. In principle, solvents with high Gutmann donor number (DN) might serve as the H-bond acceptor and thus remarkably regulate the H-bond environment of aqueous electrolytes.^[39a] Dimethylacetamide (DMA), with a high DN of 27.8, is favorable to the formation of H-bond between H_2O -DMA interaction due to abundant functional groups. Wu et al. introduced DMA into ZnSO_4 aqueous electrolytes to suppress the HER and enhance the stability and reversibility of Zn anodes (Figure 2h). The cell using the $\text{ZnSO}_4 + 10\%$ DMA mixed electrolyte displayed an ultra-long cycle life over 1900 h, which was approximately four times longer than that using bare ZnSO_4 electrolyte.^[31] Nevertheless, the practical effectiveness of high DN solvents in the hybrid aqueous electrolytes could still

restrict the overall chemical and electrochemical stability of such electrolytes towards electrode materials.

Apart from being H-bond donor, the H_2O molecules could also act as H-bond acceptor.^[43] Hence, a co-solvent serving both as H-bond acceptor and donor could be an ideal candidate to anchor H_2O molecules more effectively in aqueous electrolytes. For instance, methylurea (MU) serving as both H-bond acceptor ($=\text{C=O}$ groups) and donor ($-\text{NH}/\text{NH}_2$ groups) was employed to anchor H_2O molecules in aqueous electrolytes.^[44] This double H-bond interactions effectively broke the original H-bond network of H_2O molecules and greatly suppressed HER to 0.5 V versus Li^+/Li . The structurally asymmetric MU resulted in peculiar nanoscale core-shell-like clusters with localized super-high LiTFSI concentrations in aqueous solution (Figure 2i) thus enabling a stable charge-discharge operation of a rocking-chair $\text{NbO}_2 \parallel \text{LiMn}_2\text{O}_4$ full cell (175 Wh kg^{-1}) under a harsh electrolyte loading testing condition with no excess Li resource (N/P = 1), and no electrode precoating.^[44] H-bond anchored co-solvents provide a new solution to suppress the H_2O activity. More efforts should be made to explore hybrid electrolytes with higher H_2O content and less reactivity to ensure non-flammability and safety.

2.2. Molecular crowding electrolytes

Molecular crowding is a common phenomenon in living cells, in which H_2O activity in the aqueous solutions is substantially suppressed by molecular crowding agents through H-bond interaction between H_2O molecules and macromolecules (proteins, complex sugars, polysaccharides, etc.)^[48] (Figure 3a). Inspired by molecular crowding in living cells, Lu et al. introduced the water-miscible polymer poly(ethylene glycol) (PEG),^[46] polyethylene glycol dimethyl ether (PEGDME)^[49] into the LiTFSI- H_2O aqueous electrolytes. H_2O molecules were confined in a PEG/PEGDME crowding agent network via hydrogen bonding to decrease H_2O activity at a much reduced cost. A wide electrolyte operation window of 3.2 V was achieved in the molecular crowding electrolytes of 2 m LiTFSI-94% PEG-6% H_2O (Figure 3b). $\text{Li}_4\text{Ti}_5\text{O}_{12} \parallel \text{LiMn}_2\text{O}_4$ full cells demonstrated 300 cycles at 1°C in such molecular crowding electrolytes. Later, our group introduced the highly polar small molecule of urea and long-chain PEG400 into the LiTFSI- H_2O systems.^[50] Alternatively, we found that PEG and urea were prone to bond with Li^+ and could effectively displace H_2O molecules in the interior coordination shell. PEG in such hybrid electrolytes helped to facilitate a dense and uniform Li^+ conducting SEI layer to suppress H_2O penetration and the decomposition of aqueous electrolytes from a dynamic aspect.

This molecular crowding concept has also been extended to other aqueous devices, such as proton batteries, supercapacitors and zinc batteries.^[51] Lee et al. presented a multi-functional $\text{Zn}(\text{TfO})_2/\text{H}_2\text{O}$ -PEG electrolyte with a PEG network to change the local coordination environments of Zn ion from H_2O molecule-dominated structure to anion-dominated structure.^[47] Homogeneous Zn nucleation with (002) orientation was observed in such electrolyte, which suppressed the

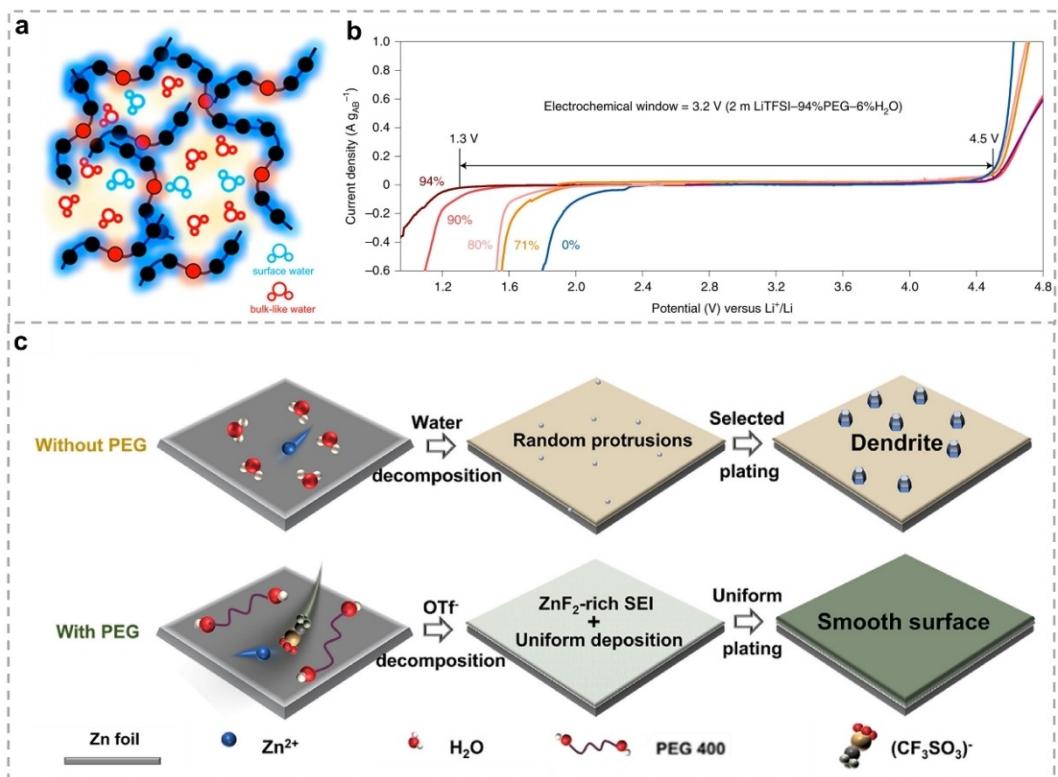


Figure 3. a) Schematic illustration of intermolecular interactions of H₂O-crowding agent. Reproduced with permission from Ref. [45]. Copyright (2020) American Chemical Society. b) Electrochemical stability windows for 2 m LiTFSI-xPEG-(1-x)H₂O ($x = 0, 71, 80, 90, 94\%$) determined by LSV tests on AB-coated aluminum foil at a scan rate of 0.2 mV s⁻¹. Reproduced with permission from Ref. [46]. Copyright (2020) Nature Publishing Group. c) Schematics of absorbed behaviors of different molecules and ions, and deposition behaviors of Zn ion on the Zn surface in the 0% and 70% PEG electrolytes. Reproduced with permission from Ref. [47]. Copyright (2022) Elsevier.

formation of Zn dendrites and other harmful by-products (Figure 3c). Symmetrical Zn|Zn cell demonstrated an ultralong cycling life of 9000 h and 8000 h at current densities of 1 and 2 mA cm⁻² in the molecular crowding 1 m Zn(TfO)₂/30 wt % H₂O–70 wt % PEG electrolyte.

Although molecular crowding electrolytes have received widespread attention in recent years, molecular crowding agents other than PEG have rarely been developed. Besides, the relatively high viscosity caused by macromolecules may deteriorate the low-temperature and high-rate performance, which needs to be further optimized.

2.3. H₂O-ionic liquids hybrid electrolytes

Ionic liquids (ILs) are novel solvents with attractive features including wide ESWs, non-flammable, high-temperature stability, and low vapor pressure. Kühnel et al. found that the LiTFSI solubility strongly increased from 21 m in H₂O (Li: H₂O = 1:2.6) to up to 60 m (Li: H₂O = 1:0.92) in the presence of hydrotropic imidazolium ionic liquid (Figure 4a).^[52] The 1LiTFSI-0.68EMImTFSI-1.38H₂O electrolyte enabled stable cycling of Li₄Ti₅O₁₂ and LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ (NCM811) electrode materials (Figure 4b). However, the low ionic conductivity of 1LiTFSI-0.68EMImTFSI-1.38 H₂O electrolytes was unsatisfactory for real

applications. Later, succinonitrile (SN) was introduced to WiSE/IL hybrid electrolytes, which led to a 2–4 folds increase of the ionic conductivity (2–4 mS cm⁻¹) while maintaining outstanding electrochemical stability. Aqueous full cells based on Li₄Ti₅O₁₂ and NCM811 were demonstrated with good cycling stability and Coulombic efficiencies close to 99.5% at 1 C.^[54] Aqueous Li₄Ti₅O₁₂||NMC811 batteries also showed improved rate performance in 1LiTFSI-1EMImTFSI-1SN-xH₂O ($x = 1, 2$) electrolytes.

Our group introduced hydrotropic ionic liquid 1-methyl-1-propylpiperidinium bis(fluorosulfonyl)imide (PP₁₃FSI) into LiTFSI-H₂O system and demonstrated an extended ESW up to 4.9 V for the aqueous electrolyte. The hydrotropic PP₁₃FSI provided the hydrophobic PP₁₃⁺ cations and lithium-philic FSI anions and thus greatly enhanced electrochemical stability (Figure 4c). The PP₁₃FSI participated in decomposition and resulted in an organic/inorganic hybrid alkaline SEI due to the isolated water-in-salt solvation structure, which thus further kinetically extended the operation window of such electrolyte at the negative voltage side.^[53] As a result, the electrochemical performance of aqueous Li₄Ti₅O₁₂||LiMn₂O₄ full cells demonstrated stable cycling over 1000 cycles at 2 C rate (Figure 4d). Though with a significant extension of ESW and cycling performance of low voltage anode materials, the use of high-

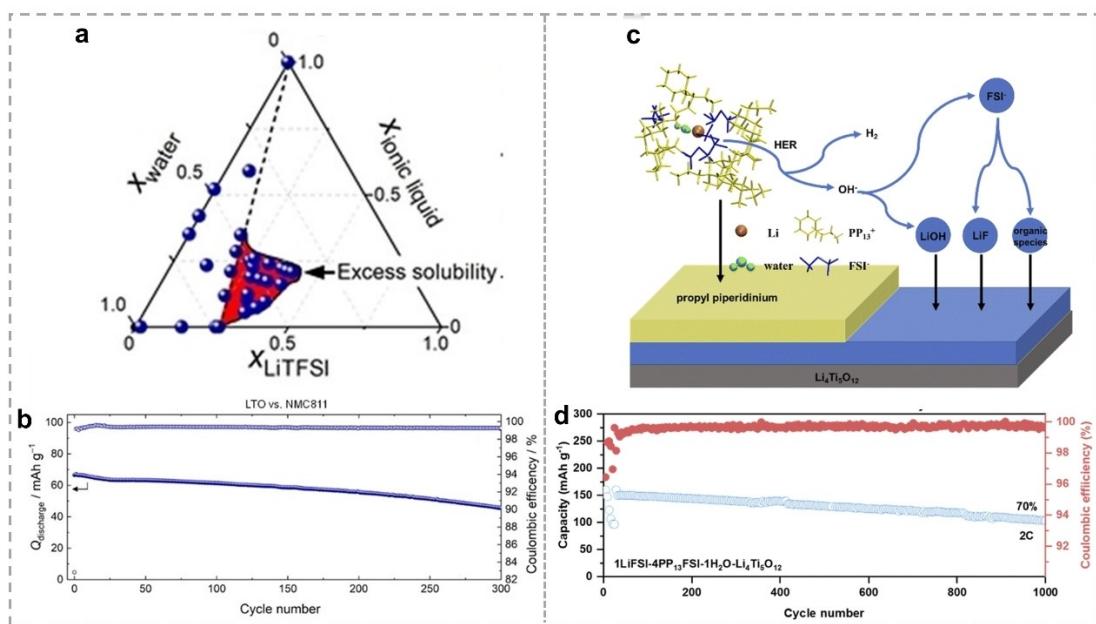


Figure 4. a) Ionic liquids boosted the LiTFSI solubility in H₂O from 21 to 60 mol kg⁻¹. Excess lithium salt solubility arose from a hydroscopic effect of the ionic liquids. b) Stable cycling of Li₄Ti₅O₁₂ | NMC811 full cells. Reproduced with permission from Ref. [52]. Copyright (2021) Wiley-VCH. c) Schematic illustration of the formation of the alkaline-based inorganic-organic mixed SEI layer on Li₄Ti₅O₁₂ electrodes in LiFSI-PP₁₃FSI-H₂O electrolytes. d) Cycling stability and CE of the Li₄Ti₅O₁₂ | LiMn₂O₄ cell using the 1LiFSI-4PP₁₃FSI-1H₂O-Li₄Ti₅O₁₂ electrolyte at 2 C. Reproduced with permission from Ref. [53]. Copyright (2022) The Royal Society of Chemistry.

cost IL in the aqueous electrolytes may present limitation for practical applications.

2.4. H₂O-deep eutectic solvents hybrid electrolytes

Different from ILs, deep eutectic solvents (DESs) are eutectic mixtures of hydrogen bond donors and acceptors that are often cheaply obtained, easily prepared, and made of relatively nontoxic and biodegradable compounds.^[55] DESs exhibit lower melting points than those of each component. Besides, DESs have functional groups that can serve as both donors and acceptors of hydrogen bonds.^[56] Therefore, DESs have been recently introduced into the aqueous electrolyte to minimize H₂O reactivity.

Xu et al. reported a non-flammable ternary deep eutectic electrolyte composed of LiTFSI-KOH-CO(NH₂)₂-H₂O with expanded ESW of >3.3 V (Figure 5a).^[32] The addition of CO(NH₂)₂ could minimize the interfacial H₂O on the anode surface and suppress the H₂O activity, thus expanding the electrochemical stability window. A small amount of KOH was added simultaneously with CO(NH₂)₂ to catalyze the reduction of the TFSI anions in order to form a LiF-rich SEI. The 1.5 mAh cm⁻² Li₄Ti₅O₁₂ | LiMn₂O₄ (103 Wh kg⁻¹) full cells exhibited 1000 cycles and >87% capacity retention at 0.5 C (Figure 5b). Besides, the LiTFSI-KOH-CO(NH₂)₂-H₂O electrolyte also enabled stable cycling of Li₄Ti₅O₁₂ | LiVPO₄F full cells with an energy density of 123 Wh kg⁻¹.

DESs also have been developed to inhibit zinc dendrites and parasitic reactions for AZIBs.^[59] Zhao et al. reported a new

"water-in-DESs electrolyte (urea/LiTFSI/Zn(TFSI)₂ (LZ-DES/nH₂O) at ambient temperature for AZIBs.^[60] H₂O molecules were confined to the LZ-DESs/nH₂O interaction network via H-bonding with TFSI and urea and embedded in the Li⁺-coordination structure (Figure 5c). As a result, these hybrid electrolytes effectively prevented side reactions and zinc dendrites. Moreover, a hydrated salt (Zn(ClO₄)₂·6H₂O) and a neutral ligand SN were mixed without additional H₂O to prepare a novel DES.^[58] The Lewis basic SN could essentially participate in the primary solvation shell of Zn²⁺, and form hydration-deficient complexes, [Zn(H₂O)₂(SN)₂]²⁺ cations, which enabled dendrite-free Zn plating/stripping behavior (Figure 5d). Besides, the portion of H₂O replaced with SN contributed to the formation of the hydrated eutectic structure, thus preventing the HER. Such electrolytes can effectively avoid the H₂O-induced side reactions, stabilize the zinc metal anodes, further improve the Zn plating/stripping CE and prolong the lifespan of Zn anodes. Compared to common aqueous solutions, the aqueous DES system is effective in promoting smooth Zn deposition and plating/stripping reversibility as well as suppressing side reactions. Hybrid DESs could be a low-cost and effective strategy to boost the development of ALIBs and AZIBs, but it is necessary to balance the more negative ESW and the slower reaction kinetics due to the more content of metal salts with high metal ions/H₂O ratio in hybrid electrolytes.

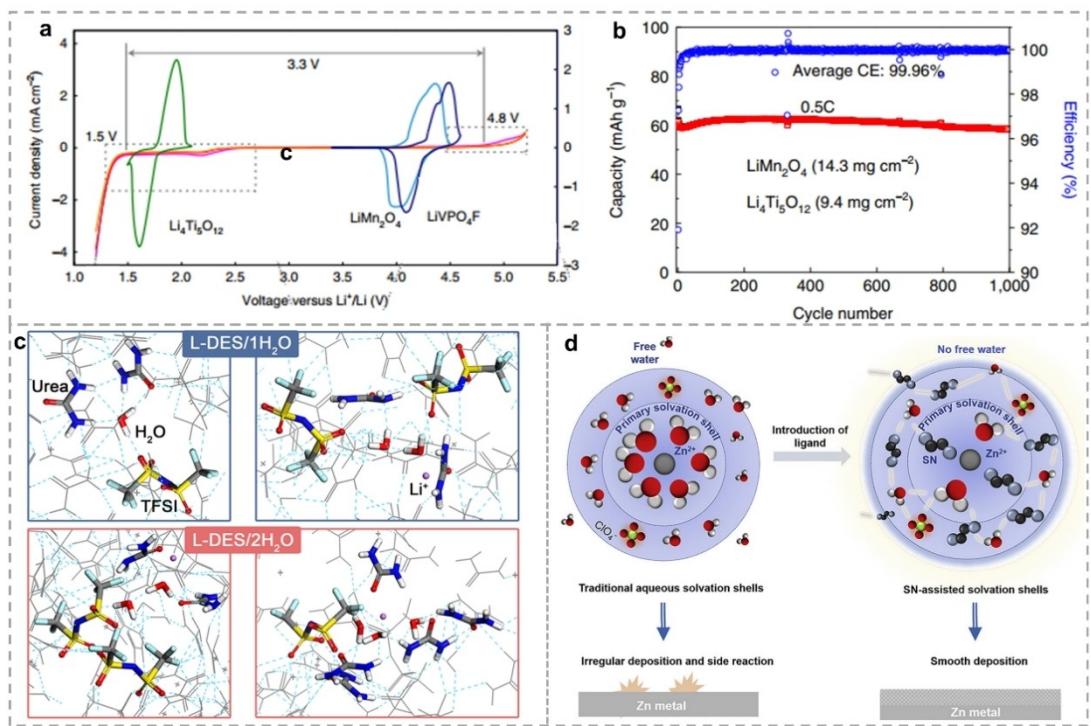


Figure 5. a) ESW of the hybrid electrolytes and redox of electrodes overlaid with cyclic voltammograms in 4.5 M electrolyte. b) The cycling stability of the $\text{Li}_4\text{Ti}_5\text{O}_{12} \parallel \text{LiMn}_2\text{O}_4$ full cell in 4.5 M electrolyte at 0.5 C. Reproduced with permission from Ref. [32]. Copyright (2022) Nature Publishing Group. c) Snapshots of electrolyte systems and representative interaction structures of H_2O molecules for L-DES/1H₂O (top) and L-DES/2H₂O (down) obtained by DFT-MD simulations. Reproduced with permission from Ref. [57]. Copyright (2022) Elsevier. d) Schematic diagrams of Zn^{2+} solvation structure and corresponding interfacial reactions in electrolytes without SN (left) and with SN (right). Reproduced with permission from Ref. [58]. Copyright (2022) Elsevier.

2.5. Gel electrolytes

Mixing the appropriate types and amounts of organic hydrophilic polymers (such as polyacrylamide, polyvinyl alcohol and gelatin, etc.) with aqueous electrolytes could form non-flammable aqueous gel electrolytes.^[61] Gel electrolytes provide another low-cost solution to restrict the activity of H_2O by forming H-bonding network in the gel matrix through the functional groups of polymers, which is beneficial to extending the ESW, alleviating gas generation, suppressing electrode material degradation and current collectors corosions in aqueous electrolytes.^[62] A broad ESW of 4.3 V with a low reduction potential below 1.0 V (vs. Li^+/Li) was achieved by combining a hydrogel electrolyte with a deep eutectic solvent in ALIBs.^[63] Besides, gel electrolytes present certain attractive attributes, such as high flexibility, desirable electrochemical properties and excellent mechanical integrity, making them suitable for both functional electrolytes and separators.^[64] Gel electrolytes have also been developed to inhibit the Zn dendrite growth and enhance electrochemical stability for AZIBs.^[65] However, the relatively low ionic conductivities of gel electrolytes lead to low rate performance and unsatisfactory power density of aqueous batteries. Besides, the polymer network in gel electrolytes lacks enough mechanical strength because improving their mechanical properties often sacrifices their ionic conductivity.^[66] Designing gel electrolytes with high ionic conductivity and high mechanical tolerance is desired for

practical use. Zhi et al. reported a hierarchically structured gel electrolyte by grafting polyacrylamide on the gelatin chain that was embedded in a network of polyacrylonitrile fiber membrane, which showed both high ionic conductivity of 17.3 mS cm^{-1} at room temperature and excellent flexibility and mechanical strength.^[67] Optimization of the close association of the polymer matrix, H_2O and the conducting salt might further extend the operating temperature range and the durability of gel electrolytes for aqueous batteries.

3. Summary and Perspectives

The innovation of advanced aqueous electrolytes is closely related to the application of rechargeable aqueous batteries. Hybrid aqueous/non-aqueous electrolytes exhibit high conductivity, low viscosity, and low cost. The use of hybrid aqueous/non-aqueous electrolytes is an effective strategy for assembling high-voltage aqueous batteries by expanding the scope of available electrode materials and increasing the energy density owing to the advantage of their wide ESWs. Although great progress on the performance of aqueous batteries using hybrid aqueous/non-aqueous electrolytes has been obtained, some main challenges still need to be faced. The mechanisms of SEI formation of hybrid electrolytes are still not clear. The practical development of hybrid aqueous/non-aqueous electrolytes is still in the laboratory research stage. Herein, we propose some

perspectives on the development of hybrid aqueous electrolytes.

- 1) **Mechanisms of SEI formation in hybrid aqueous/non-aqueous electrolytes must be further explored or optimized.** A more fundamental understanding of the solvation structure of the electrolytes and interfacial chemistries should be investigated. Besides, the fundamental studies that clear the mechanism of expanding ESW from thermodynamic and dynamic aspects are still unsettled. It should be noted that the stabilization of electrolytes on the anode side (hydrogen evolution) is much more challenging than on the cathode side (oxygen evolution) for the application of high-energy aqueous batteries. Attempts to figure out the design mystery of cation-anion-H₂O-co-solvent interactions and their correlations to the bulk and interphasial SEI properties of aqueous electrolytes are urgent.
- 2) **Systematically in-situ or operando analyses must be developed.** Currently, X-ray photoelectron spectroscopy, Raman and Fourier transform infrared spectroscopy, scanning electron microscopy, and transmission electron microscopy are used for the characterization of electrolytes and electrode interfaces. However, external factors would interfere with the ex-situ characterizations. For example, sample handling, air exposure, and beam damage (X-ray radiation/Ar⁺ sputtering exposure) may change the properties of SEI on electrodes. Thus, in-situ or operando visualization and spectral characterization with non-damage will play important roles in providing accurate and online information on interfacial chemistry. Also, in-situ techniques and characterizations can monitor the real-time dynamic changes during the electrochemical reaction process, which allows us to gain a better understanding of battery failure analysis and interphasial chemistry in aqueous batteries.
- 3) **Evaluating gravimetric energy density at the cell level.** Most hybrid electrolytes of ALIBs still have a very low H₂O content, typically < 10 wt.%, which causes an adverse impact on the viscosity and ionic conductivity of electrolytes. Increasing areal capacity to a high areal capacity for practical use leads to severe voltage polarization, lower utilization of active materials, and poor rate performance. Besides, lean electrolyte usage for aqueous batteries is required to achieve a high energy density. However, a large amount of electrolyte was employed in the reported aqueous batteries. So far, it is still challenging to reduce the aqueous electrolyte quantity owing to the decomposition of aqueous electrolytes such as hydrogen generation. Continuous efforts are needed to reduce electrolyte usage by improving the wettability between electrolytes and electrode materials, reducing electrode porosity, reducing the electrolyte viscosity, and improving electrochemical stability.
- 4) **Paying more attention to safety.** The original intention of researching aqueous batteries is their excellent safety. It is noteworthy that the property of nonflammability of the electrolyte depends on both self-extinguishing time and flash point. A simple mixture of organic species-H₂O might lose the advantage of the intrinsic safety of aqueous

electrolytes, especially under high temperatures and high-rate cycling. Rational and careful evaluation of safety issues of hybrid aqueous electrolytes should be crucial in practical applications. More detailed requirements for the nonflammability test of hybrid aqueous electrolytes should be established.

In summary, although great progress has been reached in hybrid electrolytes' research, their development potential in electrochemistry has not yet been fully explored and well understood. We believe that hybrid electrolytes are the important developing direction for aqueous electrolytes considering both cost and electrochemical performance of aqueous batteries. A future deep understanding of the hybrid aqueous systems could provide solutions for the present challenges.

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Conflict of Interest

There are no conflicts to declare.

Data Availability Statement

Research data are not shared.

Keywords: aqueous batteries • aqueous lithium-ion batteries • aqueous zinc-ion batteries • H₂O activity • hybrid electrolytes

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