REVIEW

small methods
www.small-methods.com

Electrolyte Strategies Facilitating Anion-Derived Solid-Electrolyte Interphases for Aqueous Zinc–Metal Batteries

Huihua Li, Zhen Chen, Leilei Zheng, Jian Wang, Henry Adenusi, Stefano Passerini,* and Huang Zhang**

Rechargeable aqueous zinc–metal batteries (AZBs) are a promising complimentary technology to the existing lithium-ion batteries and the re-emerging lithium–metal batteries to satisfy the increasing demands on energy storage. Despite considerable progress achieved in the past years, the fundamental understanding of the solid-electrolyte interphase (SEI) formation and how its composition influences the SEI properties are limited. This review highlights the functionalities of anion-tuned SEI on the reversibility of zinc–metal anode, with a specific emphasis on new structural insights obtained through advanced characterizations and computational techniques. Recent efforts in terms of key variables that govern the interfacial behaviors to improve the long-term stability of zinc anode, i.e., Coulombic efficiency, plating morphology, dendrite formation, and side-reactions, are comprehensively reviewed. Lastly, the remaining challenges and future perspectives are presented, providing insights into the rational design of practical high-performance AZBs.

1. Introduction

Lithium-ion batteries (LIBs) are widely used to power electronic devices and electric vehicles owing to their high energy/power densities and prolonged cycle life, while the rapid development of renewable energy resources calls for competitive technology with intrinsic safety and cost-efficiency, to reliably transmit the produced energy to power consumption.[1] Rechargeable aqueous batteries, inspired by the success of lead-acid batteries, are drawing increased attention as a complementary battery choice for energy storage, benefiting from the use of nonflammable aqueous electrolytes.[2] Recently, aqueous zinc–metal batteries (AZBs), operated by shuttling Zn^{2+} between the electrodes through aqueous electrolyte, have been intensively investigated and are expected to be a promising alternative for stationary and large-scale energy storage applications (**Figure 1**a).[3] Compared to LIBs, the salient advantages of AZBs include compatibility with mild aqueous electrolytes, high specific capacity (5854 Ah L^{-1} and 820 Ah kg^{-1}), as well as a high abundance of Zn in the Earth's crust.[4] However, several key challenges related to the Zn electrodes still impede the practical application of AZBs

---

H. Li, Z. Chen
Key Laboratory of Engineering Dielectric and Applications (Ministry of Education)
School of Electrical and Electronic Engineering
Harbin University of Science and Technology
Harbin 150080, P. R. China
E-mail: chen.zhen@hrbust.edu.cn

L. Zheng, H. Zhang
Institute of Flexible Electronics
Northwestern Polytechnical University
Xi'an 710072, P. R. China
E-mail: iamhzhang@nwpu.edu.cn

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/smtd.202300554

DOI: 10.1002/smtd.202300554

J. Wang, S. Passerini
Helmholtz Institute Ulm (HIU)
D-89081 Ulm, Germany
E-mail: stefano.passerini@kit.edu

J. Wang, S. Passerini
Karlsruhe Institute of Technology (KIT)
D-76021 Karlsruhe, Germany

H. Adenusi
Department of Chemistry
The University of Hong Kong
Hong Kong, P. R. China

H. Adenusi
Hong Kong Quantum AI Lab
Hong Kong, P. R. China

S. Passerini
Chemistry Department
Sapienza University of Rome
Rome 00185, Italy

H. Zhang
Chongqing Innovation Center
Northwestern Polytechnical University
Chongqing 401135, P. R. China

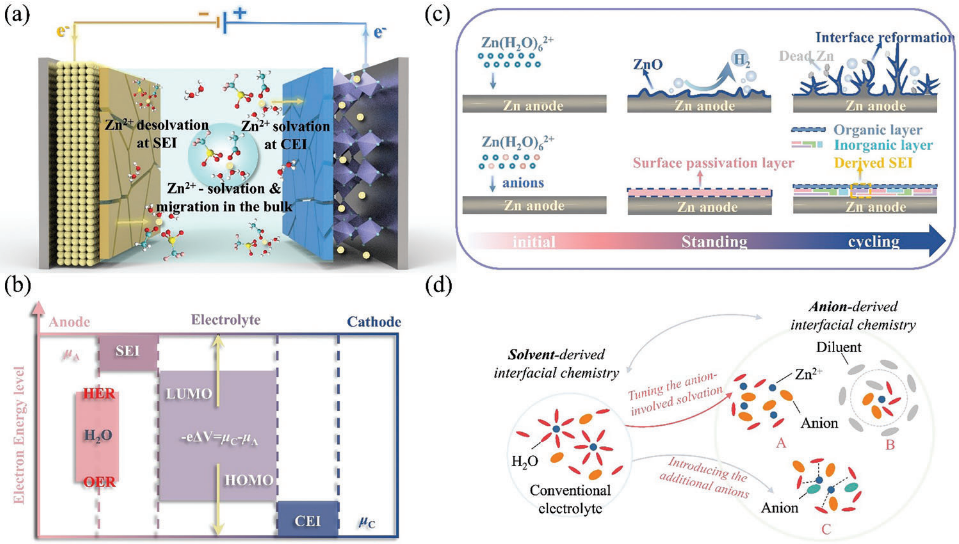


Figure 1. Aqueous zinc electrochemistry. a) Electrolytes and the associated interphases in aqueous zinc batteries. b) Expected formations of SEI on the anode and cathode in aqueous zinc batteries. The energy level difference between the redox reactions of electrodes and the HOMO/LUMO levels of electrolyte govern the thermodynamic stability and is the driving force to form the SEI and CEI layers. c) Illustration of surface evolution mechanism of Zn anode. d) Illustration of electrolyte manipulation strategies in tuning the anion-derived interfacial chemistry for aqueous Zn batteries.

technologies, such as low Coulombic efficiency (CE), thermodynamic instability of Zn metal in aqueous media inducing inevitable dissolution and side reactions, and dendrite growth during deposition, each of which has plagued the Zn reversibility since the traditional Alessandro Volta's Cu||Zn piles to current rechargeable zinc-ion batteries.[3a,5] The aforementioned challenges originate from the direct interactions between Zn metal and aqueous electrolytes.

Recently, considerable efforts have been carried out to improve the reversibility of Zn anode, such as electrode modification, and separator design.[6] However, the electrode–electrolyte interface where electrode reactions occur govern the operative cell performance.[7] In nonaqueous LIB systems, the concept of solid-electrolyte interphase (SEI) was introduced by Peled when investigating the electrochemical processes of Li metals in organic electrolytes.[8] Due to the relatively low operating potential of Li metal anodes, the electrolyte species, including solvent molecules and anions in salts, would be electrochemically reduced to generate solid products at the electrode surface, i.e., the SEI. In this context, the interphase chemistry leverages the knowledge to improve the CE, cycling life, and safety of metal anodes over the battery lifetime.[9] From the thermodynamic point of view, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the electrolytes, including both salts and solvents, determine the stability window of a battery within their potentials against oxidation and reduction, as displayed in Figure 1b.[7a,10] For instance, the reduction of the electrolyte components at anode interfaces leads to the formation of solid product layers (SEI), while the decomposition of water would passivate the surface of Zn, leading to the irreversibility. Even though it is generally accepted that a robust SEI could be formed in the organic electrolytes resulting from the synergetic decomposition of solvents and anions, to form such an SEI in aqueous electrolytes is difficult due to the relative stability of anions compared to the water molecules, i.e., the competitive hydrogen evolution reaction (HER).

Interestingly, the recent success of highly concentrated electrolyte (HCE) in aqueous batteries provides the possibility to form a stable SEI on the anode, which can inhibit the hydrogen evolution and broaden the anodic stability.[11] For example, the SEI layer is observed on Al current collector in a Li-based hydrate-melt electrolyte, due to the formation of ion pairs when anions are contacting the Li^+, which can regulate the LUMO energy level of anions from salts.[12] Although this passivated layer is soluble to some extent in a free water enrichment environment, the HCEs, in which most of the water molecules are coordinated with Li^+, can retain its structure. In AZBs, the formation of a robust SEI layer that is ionically conductive to Zn^{2+} but electronically insulating, is also expected to be valid for stabilizing the electrodes and enhancing the overall cell performance.[13] Practically, adjusting the solvation structure of Zn^{2+} in the aqueous electrolyte can effectively shift the routine interfacial chemistry based on water decomposition (i.e., HER) to the electrochemical reduction of anions from salts, resulting in the anion-derived interfacial chemistry.[14] Such anion-derived SEI with desired characteristics provides powerful support to overcome the distinct dilemma of Zn metal anodes, such as poor cycling life, and low rechargeability.[9b,15] Therefore, understanding the correlation between the performance of Zn anode and the electrolyte structure, which influence the growth, composition, microstructure, and properties of the SEI layers, is crucial for developing advanced electrolytes toward the design of stable and efficient AZBs.

In this review, we focus on electrolyte strategies for the formation of anion-derived SEI layers in AZBs, in terms of the growth mechanism, compositions, and functionalities on the Zn metal electrodes. The multiple characteristics of anion-derived SEI are first presented to provide a comprehensive landscape for improving the reversibility of Zn anode. Three conventional types of electrolyte systems, namely, (localized) HCEs, hydrated eutectic electrolytes (HEEs), hydrogel electrolytes, and molecular crowding electrolytes (MCEs), are discussed along with their unique interfacial chemistries in AZBs. Moreover, additive strategies to tailor the solvation structure to facilitate anion decomposition to regulate the SEI are introduced. Lastly, future challenges and perspectives in designing stable Zn metal interfaces for practical high-performance AZBs are discussed.

2. Fundamentals of the SEI in AZBs

The current development of AZBs focus on exploring high-performance electrode materials (including both anode and cathode) to unravel their functional mechanisms.[16] However, the reversibility of metallic Zn anode is still in its infancy for implementation in practical applications. The Zn anode suffers from severe problems such as dendrite growth and side reactions (mainly related to the passivation and hydrogen evolution) in mild electrolytes (Figure 1c). In this respect, the Zn dendrites may pierce the separator and lead to short circuit of the battery. Additionally, the dendrites may detach from the bulk electrode, and form “dead zinc” which would further reduce the reversibility and efficiency of the Zn anode.[17] Meanwhile, the side reactions inevitably passivate the Zn surface by insoluble by-products and generate hydrogen gas,[18] causing the increase in electrode polarization and internal pressure. Eventually, these not only would result in the degradation of battery performance, but also trigger safety hazards.

In AZBs, the reversibility of the Zn plating/stripping process strongly depends on the nature of electrolytes and interphases. To solve the Zn dendrite growth issue, building a protective SEI layer on metal anode is a promising strategy.[15a] In principle, an ideal SEI in AZBs should possess the following characteristics, such as high electrical resistance, high Zn^{2+} conductivity and permeability, high mechanical and chemical stability, and low solubility in aqueous electrolyte at various operating temperatures and potentials.[19] The formation of the SEI would affect the divalent Zn^{2+} transportation from the electrolyte to the electrode. The Zn^{2+} transport (prior to the storage into the electrode) undergoes three general steps, including the desolvation of Zn^{2+} on the electrode surface, the migration of Zn^{2+} through the interphase, and solid-state diffusion in the bulk electrolyte. Among them, the desolvation behaviors of Zn^{2+} at the SEI are recognized as the rate-determining step, which are critical to the whole electrochemical reaction. Owing to these intrinsic difficulties, designing an SEI, which allows for fast Zn^{2+} transport kinetics and regulates uniform Zn deposition underneath the SEI layers is challenging.

Aiming to tackle the low ionic conductivity of conventional SEI, researchers have proposed building artificial interfacial layers with zincophilic and hydrophobic features are effective strategies. The ZnS or ZnF_2 artificial SEI layers have been fabricated on zinc metal to extend cycle life,[20] originating from the decreased nucleation overpotential of Zn plating as well as enhanced charge transfer kinetics at the interface, homogenized Zn nucleation/deposition behaviors, and inhibited side reactions. Specifically, a coating strategy using a polydopamine (PDA) layer was developed for efficient Zn anode in aqueous electrolyte.[21] The abundant hydrophobic groups in PDA can regulate the Zn deposition by enhanced interfacial contact, thus significantly improving the reversibility of Zn anode. Besides, carbon materials have also been widely used as substrates, coating layers, and even electrolyte additives to mitigate the irreversibility issues of Zn anode in terms of dendrite growth, corrosion, hydrogen evolution, and passivation.[22] Recently, a robust organic–inorganic hybrid artificial interphase was in situ built on Zn metal by electrochemically precycling Zn metal in the organic electrolyte (i.e., 1 M (molarity, mol L^{-1}) $Zn(OTf)_2$ in triethyl phosphate (TEP).[23] The preformed artificial interphase layer features an organic/inorganic-layered structure (consisting of $Zn_3(PO_4)_2$, ZnF_2, and ZnS in the inner layer), which generates from the decomposition of solvent and anion in the organic electrolyte. Such an artificial interphase is also effective to isolate the oxidizable Zn metal from the aqueous electrolyte and enable a highly reversible Zn anode in aqueous systems. However, although the artificial SEI coatings can improve the reversibility of Zn anode, the processing complexity and inferior mechanical adhesion to the Zn metal should be considered during the design of robust SEI, which are also crucial for the practical implementation.

Currently, the capability for an electrolyte to decompose to in situ form an efficient SEI on Zn metal anode has attracted increased attention, and these in situ formed SEI approaches further enrich the interfacial chemistry in aqueous batteries. However, different from the interfacial chemistry in organic electrolytes, which has been widely adopted to protect the Li, Na, and K metal anodes, it is difficult to build an electrolyte-derived and efficient SEI layer on Zn anode. This is predominantly due to the exceptional electrochemical stability of the conventionally used salt anions in aqueous electrolytes beyond the high redox potential of Zn^{2+}/Zn (−0.76 V vs standard hydrogen electrode) and high hydrogen evolution potential of water. Rationally modifying the electrolyte structure by an anion receptor was proposed, enabling the reduction of anions and consequently the formation of an anion-derived SEI layer.[24] In the tuned structure, the introduced anions participate in the primary solvation sheath of Zn^{2+}, forming unique structures containing contact ion pairs (CIPs) and aggregates (AGGs). Such direct interaction of cations–anions would regulate the LUMO of electrolytes which would be determined by the anions and give rise to anion decomposition. Moreover, the species in the SEI layer can be regulated by the anion composition and structure, known as the flexibility of anion-derived SEI design. The detailed strategies from an electrolyte point of view are illustrated in Figure 1d. Tuning the solvation structure through the addition of anions as active receptors in the aqueous electrolytes could successfully transition the interfacial chemistry from a solvent-derived to an anion-derived one.

3. Strategies Facilitating the Anion-Derived SEI

It has been established that the interfacial chemistry is strongly affected by the properties of the electrolytes.[9a,25] Generally, cations are coordinated by high polar solvents to form the typical solvation structure in a dilute electrolyte, in which anions are mostly excluded from the solvation structure. The conventional solvation structure in $Zn[H_2O]_6^{2+}$ without anion participation will result in competitive water decomposition concomitantly with HER, which will change the local pH and accelerate the passivation of the zinc anode by the inorganic byproducts of hydroxides or zincates.[26] Such passivated layer with electronic and ionic insulation characteristic blocks the interfacial transport of Zn^{2+} and inhomogeneous charge distribution on the electrode, causing dendrite growth and CE deterioration. Moreover, the reactant water molecules connected by the hydrogen bond network in the bulk electrolyte will facilitate the hydrogen evolution reaction,[27] making the reversibility worse. On the other hand, the solvating capability of anions can also be regulated by the cosolvent, in which the weak solvent–cation interaction will increase the portion of cation–anion coordination, thus changing the solvation structure of Zn^{2+} and facilitating the anion-derived interfacial chemistry.[24c] In conventional LIBs, a pure nonpolar solvent, namely, 1,4-dioxane, is proposed to modulate the solvation structure of Li^+, in which anions thermodynamically participate in the inner solvation sheath of Li^+ at relatively low concentrations and electrochemically reduce to form anion-derived SEI layers.[28] In general, the species participating in the primary solvation sheath of cations manifest the potential to be reduced, contributing to SEI formation. As a result, anions with distinct solvation structures in different electrolyte systems are expected to be preferentially reduced before the decomposition of water to generate an anion-derived SEI.[29]

3.1. Concentrated Electrolytes

One way to modulate the ion-solvation shell is to simply increase the salt concentration. Changes in concentration strongly affect the electrolyte properties, including the ion transport behavior, and the interfacial reaction.[30] However, in aqueous electrolytes with low salt concentrations, the decomposition of water molecules, i.e., hydrogen evolution on the anode, induces the passivation of Zn anode, making them unfeasible for the formation of desirable SEI due to the higher electrochemical stability of the anions. Moreover, the presence of uncoordinated water molecules will react with the metallic Zn, further corroding the electrode.[4b] In HCEs, there are almost no free solvent molecules, and a considerable portion of anions are participating in the solvation structure of cations.[11b,31] Therefore, the presence of the cation–anion interactions favors the reductive decomposition of the anions from salt, thus contributing to the subsequent anion-derived SEI formation.[32] By contrast, in "low concentration" electrolytes (normally less than 3 mol L^{-1} in molarity), cations are fully solvated by solvent coordination without anions competing in the coordination shell.[33]

The high concentration strategy has also been suggested to address the irreversibility issue of Zn electrodes in aqueous electrolytes. As an example, the aqueous HCE consisting of 1 m $Zn(TFSI)_2$ and 20 m LiTFSI (m: molality, mol kg^{-1}; TFSI: bis(trifluoromethanesulfonyl)imide), was initially investigated to promote the reversibility of Zn anode.[35] The postmortem analysis combined with theoretical modeling suggested the improved Zn reversibility in this electrolyte stems from the unique solvation structure of Zn^{2+}, where the high population of anions in the bulk electrolyte restricts the species to the coordination shell of Zn^{2+} to form CIPs $(Zn–TFSI)^+$ that significantly suppress the presence of $(Zn–(H_2O)_6)^{2+}$. Nevertheless, the SEI on the Zn anode was not observed. However, in a fluorine-free, concentrated dual-cation electrolyte, a unique interphasial layer was identified (**Figure 2**).[34] In this HCE, i.e., 0.5 m $Zn(ClO_4)_2$ with 18 m $NaClO_4$, the solvation structures are intrinsically changed, causing the significantly increased ratio of CIPs and AGGs species, and the free water molecules are drastically decreased. Meanwhile, the electronic state of the electrolyte is governed by the contribution of ClO_4^- in both the LUMO and the HOMO levels, in which the coordination of anions to cations leads to a dominant contribution of ClO_4^- in both LUMO and HOMO levels, due to the extensive coordination of water to cations leading to the downshift of the orbital levels of ClO_4^- anions. As a result, ClO_4^- is preferentially reduced to yield an anion-derived passivation layer. As a result, the anion-derived Cl^--rich passivation layer exhibits a low interfacial resistance, enabling the high reversibility of Zn anode, with facilitated kinetics for Zn plating/stripping and prohibiting parasitic reactions.

Fluorine-containing salts have also been used for AZBs, which can be decomposed on the Zn metal to enable the formation of SEI layer composed of fluorinated components. In an HCE with dual F-containing salts, i.e., 1 m $Zn(OTf)_2$ with 20 m LiTFSI, molecular dynamics (MD) simulations have proven that Zn^{2+} will be preferentially coordinated with $TFSI^-$ anion and partially replace the H_2O molecule in this HCE, which favors the formation of a robust anion-derived SEI layer.[36] XPS characterization evidences the presence of organic fluorine-containing species on the surface of Zn originating from the anion decomposition in HCE, while the O–H from the free water was the dominant component after cycling in low concentration electrolyte (LCE). The anion-derived SEI acts as the main passivation layer on the electrode in HCE, which is different from the one in LCE and contributes to cell performance with higher stability. Even though, the fluorine-containing species, which are widely recognized as robust SEI components, were not reported.

Considering the increased cost of concentrated salts in HCEs for practical applications, the future direction should focus on the development of salt with functional anions which can be easily decomposed to form a protective SEI in a relatively low concentration. For example, the sulfamate anion can easily adsorb on the oxidizable metal anode to build an anion-rich Helmholtz plane. Due to a lower LUMO energy, the sulfamate anions $(NH_2SO_3^-)$ at a relatively low concentration (less than 3 M) can be preferentially reduced to generate a stable composite SEI with a mixture of ZnS, $ZnSO_3$, Zn_xNO_y, and $ZnCO_3$ species to suppress the parasitic side reactions on the Zn metal anode.[37] On the other hand, introducing low-cost dilute solvent in HCEs would be an alternative efficient strategy to lower the overall cost of the electrolyte, maintaining their general properties. Urea was introduced into the HCE of 21 m LiTFSI "water-in-salt (WIS)" electrolyte, aiming to modulate the interfacial chemistry.[38] Robust anion-derived SEI and cathode electrolyte interphase (CEI) layers were detected on the surface of anode and cathode, respectively, which can effectively inhibit the dissolution of electrode materials in aqueous media due to their robust structure with amorphous organic–inorganic components. Such unique interfacial chemistry enabled by dilute strategy provides a new direction for designing affordable and efficient electrolytes for AZBs.

Localized highly concentrated electrolytes (LHCEs) offer a possible dilution strategy for HCEs. The introduction of low-polarity inert cosolvent as diluent will barely impact the intrinsically electrochemical properties of the HCE but remarkably lower the

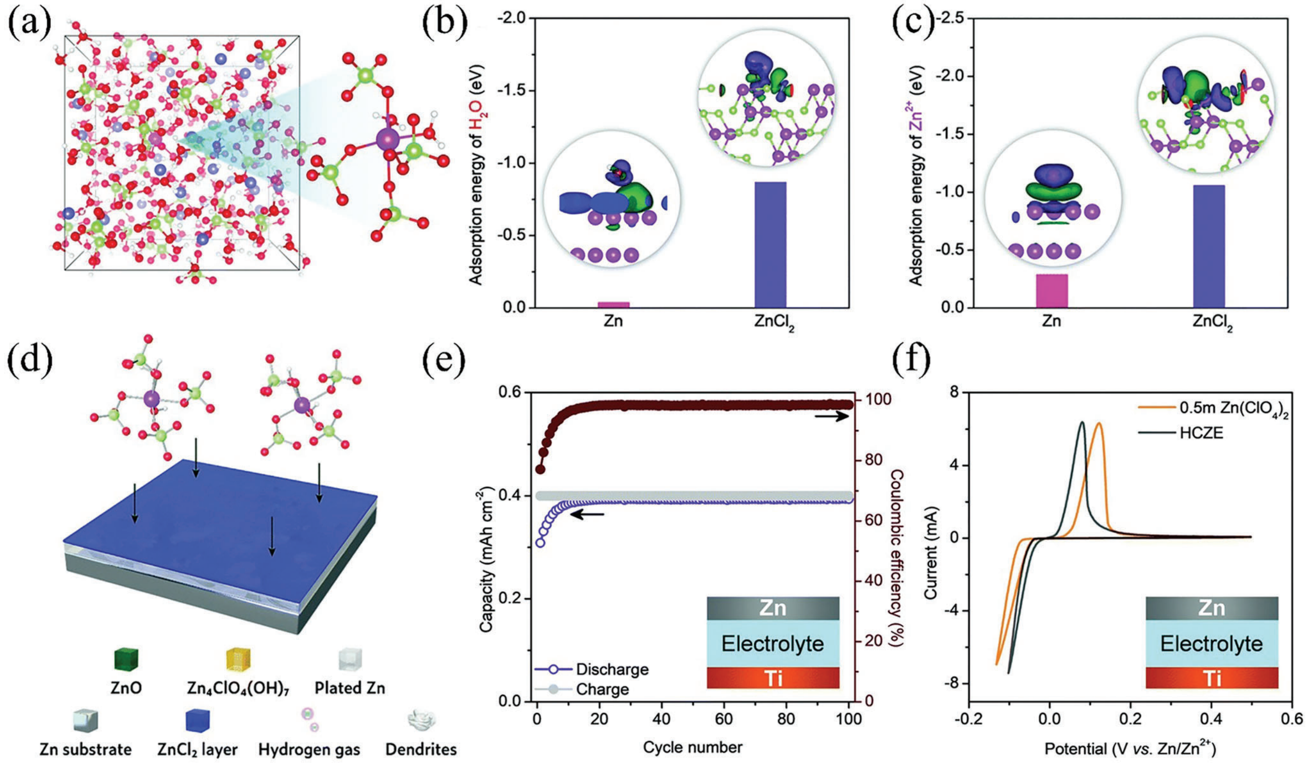


Figure 2. Concentrated aqueous electrolytes for Zn anode. a) Snapshots of the simulated solvation structures from MD simulations in a 0.5 m $Zn(ClO_4)_2$ + 18 m $NaClO_4$ aqueous electrolyte. b) H_2O and c) Zn^{2+} adsorption energies on the Zn and $ZnCl_2$. d) Schematic illustrations of Zn^{2+} solvation structures and formation of SEI layer. e) CE of Zn plating/stripping processes upon cycling on Ti as working electrode at 0.4 mA cm^{-2}. f) CV curves of Zn plating/stripping using dilute and concentrated electrolytes at a scan rate of 1 mV s^{-1}. Reproduced with permission.[34] Copyright 2021, The Royal Society of Chemistry.

viscosity of the solution and, to a large extent, increase the ionic conductivity.[40] In LHCEs, the salt anion should have high coordination ability or multiple "docking stations" in its molecular structure to avoid precipitation in a relatively high salt-to-solvent ratio. For example, the cyclic ether, 1,3-dioxane (DX), exhibits a low dielectric constant (ϵ) value with weak solvating power due to the steric effect, which has been proven to be a promising dilute solvent to form LHCE. Typically, the analogue of 1,4-DX exhibits a much lower ϵ value (2.2), which is even lower than that of benzene ($\epsilon = 2.3$), hence it is a superior nonpolar solvent with an extremely weak solvating ability. The use of 1,3-DX and 1,4-DX as cosolvents would reduce the solvating ability and force the formation of more ion pairs, e.g., cation–anion interactions.[28] In view of this, LHCEs possess similar solvation structure as HCEs, while the salt-to-solvent ratio can be decreased to some extent and the ionic conductivity can be largely enhanced due to the reduced viscosity. In this respect, the anion-derived interfacial behavior can be retained without sacrificing the electrochemical properties of the electrolyte.

An aqueous LHCE with 1,4-DX as the dilute cosolvent in aqueous HCE (1 m $Zn(TFSI)_2$ + 19 m LiTFSI + 9 m LiBETI) was designed for Zn anode to address the reversibility issue (**Figure 3**).[39] The unique solvation structure in the LHCE with the water-to-1,4-DX molar ratio of 1:3 as solvent significantly facilitates the anion-derived interfacial chemistries to form fluorine-containing interphases. Moreover, the 1,4-DX also acts as hydrogen bond modulator and reduces water reactivity. As a result, the LHCE enables a high CE quickly reaching an average value of 99.7% (higher than that of conventional HCE) and dendrite-free deposition behavior for Zn anode, which enables higher rate capability and cycling stability in Zn||V_2O_5 batteries. Besides, ethylene glycol (EG) is also proposed as additional water blocker to form LHCE for AZBs.[41] The participation of EG molecules in the solvation structure strongly inhibits the water reactivity, decreases the formation of hydrate products, and strengthens the close interaction between Zn^{2+} and SO_4^{2-}, which suppresses the hydrogen evolution and uniformizes the Zn plating/stripping reaction. Benefiting from this electrolyte, a full cell using Zn as anode and phenanthrenequinone macrocyclic trimer as cathode demonstrates an extremely long cycling life (up to 8000 cycles). Furthermore, this electrolyte is nonflammable without using expensive precursors and stable when exposed to air atmosphere, providing a feasible solution to utilize HCEs for practical AZBs applications.

Besides the dilution strategy, the microstructure design of the electrode can also encourage the design of LHCEs in the vicinity of the electrode by regulating the space charge distribution.[42] The use of a 3D nanoporous Zn electrode enables the formation of an interface-LHCE via the space charge effect in the nanopore structure. Consequently, the Zn electrode exhibits high reversibility for 750 h during the stripping/plating test, due to the uniform deposition behavior of Zn and suppressed side

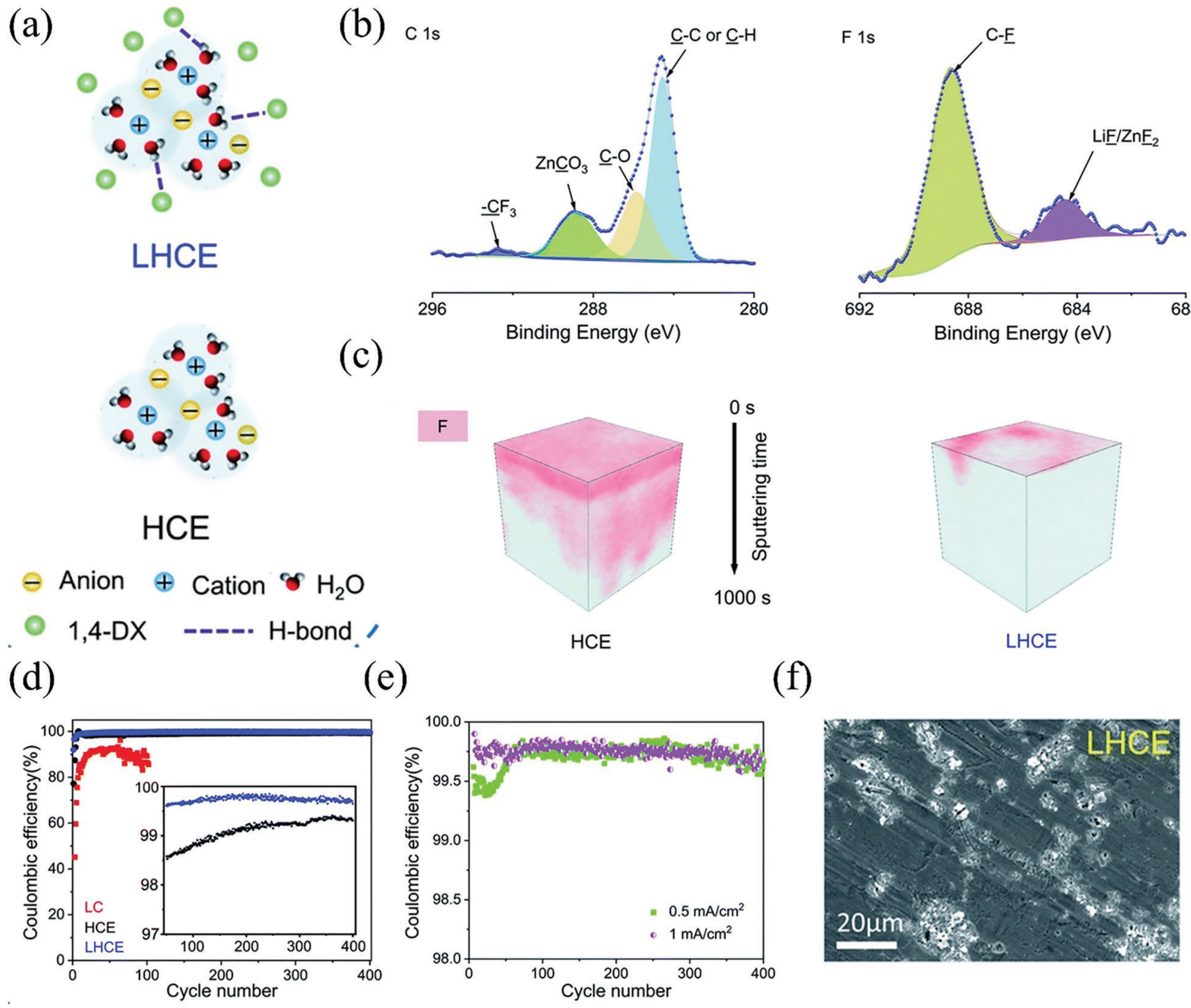


Figure 3. Localized concentrated aqueous electrolytes for Zn anode. a) The schematic illustration of solvation structures in aqueous electrolytes (HCE: $(TFSI)_{0.7}(BETI)_{0.3}$, LHCE: $(TFSI)_{0.7}(BETI)_{0.3}$ in a mixture solvent with a water/1,4-DX molar ratio of 1:3). b) XPS spectra of C 1s and F 1s recorded on Zn metal after cycling in LHCE. c) ToF-SIMS 3D view of F elements distributions of SEI in HCE and LHCE. d) CEs of Zn plating/stripping upon cycling in various aqueous electrolytes at 0.2 mA cm^{-2} and 0.2 mAh cm^{-2} (LC: 1 m $Zn(TFSI)_2$). e) CEs of Zn plating/stripping upon cycling in the LHCE at 0.5 and 1 mA cm^{-2}. f) SEM image performed on cycled Zn anode at 0.2 mA cm^{-2} and 0.2 mAh cm^{-2}. Reproduced with permission.[39] Copyright 2021, The Royal Society of Chemistry.

reaction, which is superior to the pristine Zn foil electrode. The full cell coupled with a $NaVO_3$ cathode exhibits a significantly improved lifespan with higher capacity retention. Based on this concept, the molecular sieves with ordered mesoporous structures can also be used as localized environments to confine the water molecules and construct the LHCE on the surface of electrode.[43] It has been reported that these solvation structures are strongly affected by the pore diameters of the molecular sieves, in which a protective layer using mesoporous molecular sieves (MCM41) in a channel diameter of 2.5 nm successfully promotes the formation of an LHCE with a lower Zn^{2+} desolvation energy. The redistribution of the electric field and concentration gradient at the electrode surface can efficiently regulate the Zn deposition behavior. Consequently, the resultant MCM41-coated Zn electrode delivers improved cycling stability during Zn stripping/plating process compared with the pristine Zn electrode. These results indicate that the electrolyte approaches involve tuning the intrinsic solvation structure by enhancing the association of cations and anions, which can efficiently boost the anion-derived interfacial chemistry. Due to the presence of weakly solvating solvent, anions are competing to enter the primary solvation structure of Zn^{2+}, therefore the cation–anion interaction can theoretically give rise to the anion-derived interfacial chemistry.

3.2. Hydrated Eutectic Electrolytes

As new versatile and green electrolyte materials, the deep eutectic solvents (DESs) are generally formed through strong ion–dipole interaction in a mixture of Lewis or Brønsted acid and base with

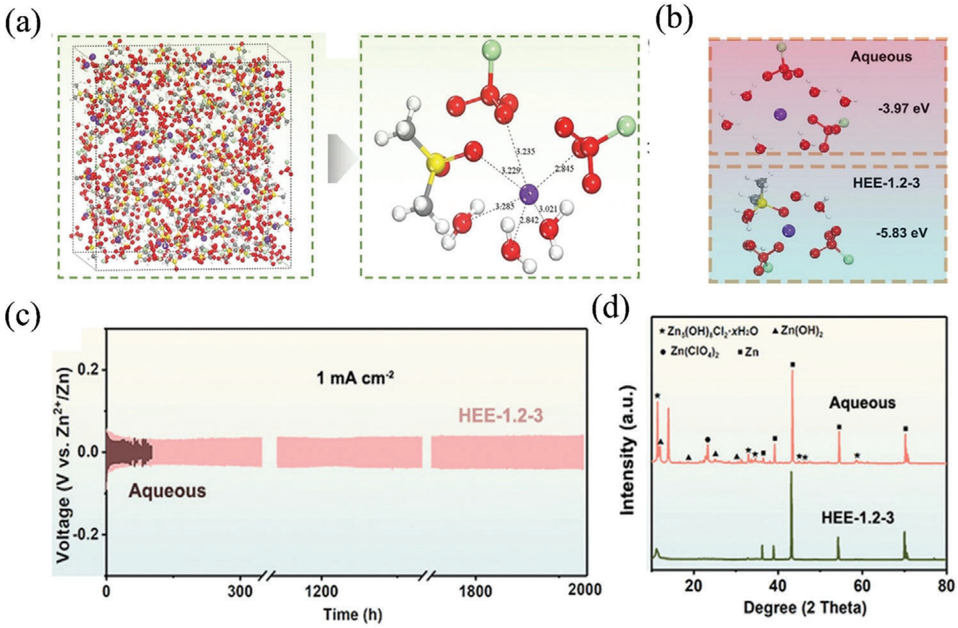


Figure 4. Hydrated eutectic electrolyte for Zn anode with improved reversibility. a) A snapshot obtained by MD simulations and dominant Zn^{2+}-solvation structure of HEE-1.2-3 solution. b) Calculated total binding energy of typical Zn^{2+}-solvation structures in aqueous and HEE-1.2-3 electrolytes. c) Voltage profiles of Zn||Zn symmetric cells upon cycling in aqueous and HEE-1.2-3 electrolytes. d) XRD patterns collected on the cycled Zn electrodes in different electrolytes. Reproduced with permission.[47] Copyright 2022, Wiley-VCH.

a melting point lower than each individual component.[44] In the metal finishing industry, it has been confirmed that the Zn metal electrodeposited from DESs tends to have a more uniform and compact microstructure, while the Zn tends to form in a dendritic structure when deposited from aqueous electrolyte without strong base additives, which affords technological guidance for battery applications.[45] For example, Zn-based DES can be prepared by mixing conventional Zn salts such as $ZnCl_2$, $Zn(OTf)_2$, $Zn(ClO_4)_2{\cdot}6H_2O$ with organic ligands such as choline chloride, ethylene glycol (EG), urea, acetamide, and *N*-methylacetamide. These DESs demonstrate intrinsically promising capabilities and compatibilities as electrolyte materials for AZBs due to their high stability in moist air and water-miscibility.[46]

HEEs can be prepared by directly mixing the hydrated salts (e.g., $Zn(ClO_4)_2{\cdot}6H_2O$ or $Mg(NO_3)_2{\cdot}6H_2O$) into the above organic ligands.[48] In the presence of water, the aqueous DES triggers the deep eutectic effect due to the weak hydrogen bonds interruption and biased reconstruction of H_2O to form the water-containing eutectic mixtures, displaying distinct advantages when applied in AZBs. Since the water molecules have a lower energy barrier than that of the organic ligands during the desolvation process, the nucleation overpotentials for Zn deposition are reduced by manipulating the Zn^{2+} solvation structure. Thus, the formed "water-in-HEE" structure increase the ionic diffusion ability, and enhance the kinetics for Zn^{2+} deposition, which is of particular interest in low temperature battery applications.[49] In light of these achievements, a notable "water-in-DES" electrolyte based on $ZnCl_2$-acetamide/H_2O components enables homogeneous Zn nucleation behavior due to the rapid desolvation kinetics of the as-formed $[ZnCl(acetamide)_2(H_2O)]^+$ cationic complex.[50] In AZB systems, an optimized HEE (i.e., HEE-1.2-3) containing $Zn(ClO_4)_2{\cdot}6H_2O$, methylsulfonylmethane (MSM) and water (in a molar ratio of 1.2:3.6:3) is proposed to improve the reversibility of Zn anode, in which the MSM (Lewis base) occurs in the vicinity of Zn^{2+} (Lewis acid) resulting in the formation of the Zn–(MSM)–(H_2O) solvation structure (**Figure 4**).[47] A higher binding energy of Zn^{2+}–MSM (−5.93 eV) indicates the tendency of MSM to access the primary solvation sheath of Zn^{2+}. The longer cycling stability of galvanostatic Zn stripping–plating in symmetric cell was achieved in the HEE-1.2-3 electrolyte than the baseline electrolyte, due to the suppressed by-product formation. As a direct proof-of-concept, a new HEE by directly dissolving a hydrated Zn salt ($Zn(ClO_4)_2{\cdot}6H_2O$) into a neutral organic ligand solvent (succinonitrile, SN) was investigated for use with Zn metal anode.[51] The Lewis basic SN molecule essentially participates into the primary solvation sheath of Zn^{2+} and forms a hydration-deficient complex of $[Zn(H_2O)_x(SN)_y]^{2+}$. This will reduce the affinity between Zn^{2+} and water and inhibit the parasitic reactions at the electrode/electrolyte interface. Thus, the hydrous organic electrolyte with a mixture of $Zn(ClO_4)_2{\cdot}6H_2O$:SN in a molar ratio of 1:8 significantly boosts the reversibility of Zn for plating/stripping test and enables an average CE of 98.4% upon cycling.

It has been reported that the solvation structure of cations in the HEEs can be modulated by forming a coordinated cationic complex, while the detailed investigation on the SEI in a eutectic electrolyte is still in its infancy. The HEE system normally utilizes the $Zn(ClO_4)_2{\cdot}6H_2O$ as the Zn salts, thus the chloride-based passivation layer is revealed at the interface. As proved in an acetamide-based DES system with dual salts ($LiClO_4$ and $ZnCl_2$), the electrolyte properties can be tuned by adjusting the solvent composition (i.e., the ratio of water to acetonitrile).[53]

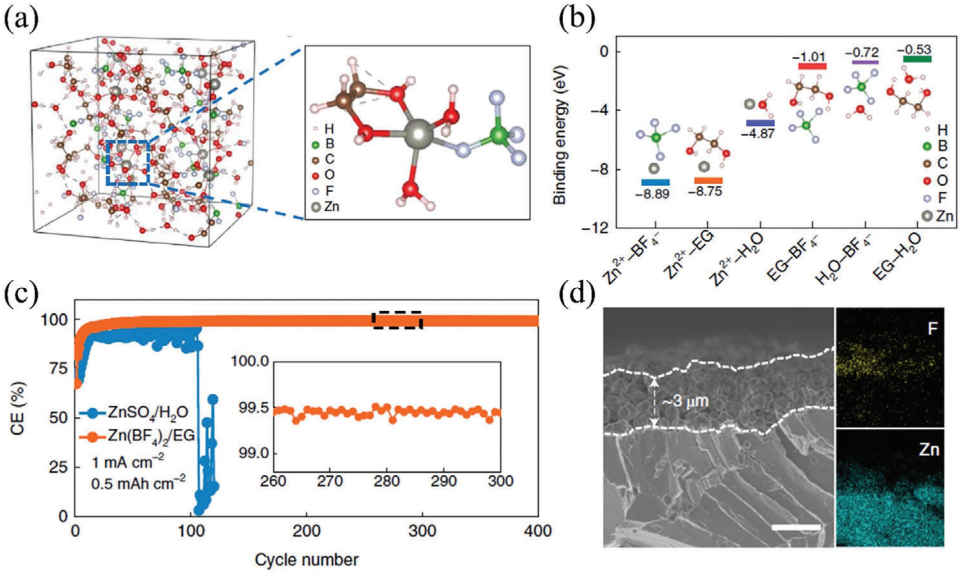


Figure 5. Hydrated eutectic electrolyte for Zn anode with unique SEI formation. a) A snapshot of the 4 m $Zn(BF_4)_2$/EG electrolyte and Zn^{2+}-solvation structure obtained from the MD simulation. b) The calculated binding energies between any two species in the $Zn(BF_4)_2$/EG electrolyte based on DFT calculations. c) CEs of Zn plating/stripping upon cycling at 1 mA cm^{-2} and 0.5 mAh cm^{-2} in different electrolytes. d) Cross-sectional SEM image collected on the Zn electrode immersed in the electrolyte for 7 days and its EDX mapping results. Scale bar is 2 µm. Reproduced with permission.[52] Copyright 2021, Springer Nature.

The addition of acetonitrile facilitates the formation of an SEI with organic/inorganic hybrid structure on the Zn anode through the synergetic decomposition reaction of acetamide, $LiClO_4$, and $ZnCl_2$ species. The presence of the SEI enhances the reversibility and stability of Zn electrode by suppressing side reactions and dendrite growth.

Another more economical and nonflammable hydrous organic electrolyte was reported consisting of a hydrated $Zn(BF_4)_2{\cdot}4.5H_2O$ salt and an EG solvent, which enables the Zn anode high stability at a high depth-of-discharge (50%) (**Figure 5**).[52] An in situ formed ZnF_2-dominant passivation layer was identified on the Zn metal soaked in the 4 m $Zn(BF_4)_2$/EG electrolyte, resulting from the decomposition of BF_4^- anions. Such dense and stable SEI can protect the Zn electrode without occurrence of dendrites and side reactions when operating at various temperatures from −30 to 40 °C. The as-fabricated full-cell using V_2O_5 as cathode also displays superior electrochemical performance than that in aqueous $ZnSO_4$ electrolyte. Similarly, a hydrous organic electrolyte by dissolving the hydrated $Zn(BF_4)_2{\cdot}5.2H_2O$ salt in nonflammable trimethyl phosphate (TMP) as solvent was also reported and demonstrated a high feasibility for reversible Zn batteries.[54] In the as-prepared 1 m $Zn(BF_4)_2{\cdot}5.2H_2O$/TMP electrolyte, the reversibility of Zn for stripping–plating reaction can be improved. Moreover, such electrolyte composition with only crystalline water from salts can reduce the water reactivity and expand the stability window of the electrolyte up to 3 V (vs Zn^{2+}/Zn). Thus, the preferential decomposition of both TMP and anions leads to the in situ formation of a $ZnF_2/Zn_3(PO_4)_2$-rich SEI on the Zn.

In principle, the interphasial chemistry in eutectic electrolytes can be realized by solvation structure manipulation, which can change the energy level of electrolyte by anions or solvents, due to the adjustable dissociation energy and complex structure. These properties will eventually guide the SEI formation process and determine its composition depending on the decomposition sequence of electrolyte constituents at the corresponding potentials. In nonaqueous Zn batteries, a ZnF_2-rich organic/inorganic hybrid structure has been detected in the SEI on Zn anode cycled in the acetamide-based eutectic electrolyte, due to the presence of $TFSI^-$–Zn^{2+} interaction. This results in a remarkable change of the $TFSI^-$ anion coordination environment and provides the preferential reduction of anions before solvents.[55] The modulated solvation structures with Zn^{2+}–$TFSI^-$ interactions generate anion-derived SEI in DES, which has already been observed in a $TFSI^-$-based "WIS" electrolyte, as reflected by the characteristic components of ZnF_2 and organic compounds from the stepwise decomposition of anions in SEI structure.[56]

3.3. Hydrogel and Molecular Crowding Electrolytes

Recently, hydrogel electrolytes have been widely investigated due to their potential applications in flexible devices.[57] In the hydrogel electrolytes, the H_2O-saturated framework with crosslinked hydrophilic polymer frameworks construct efficient 3D channels for fast Zn^{2+} transport and provides high mechanical elasticity to accommodate dendrite growth.[58] In addition, the Zn salt (or additive) and polymer structures enable the tunable properties of the electrolytes, to meet the specific application requirements.[59] Interestingly, hydrogels are capable of constructing a unique interface as artificial interphases to protect the Zn metal anode in aqueous batteries. For example, gelatin is hydrophilic and widely used as polymer framework in hydrogel. By coating crosslinked gelatin on Zn metal anode, the artificial SEI layer after the

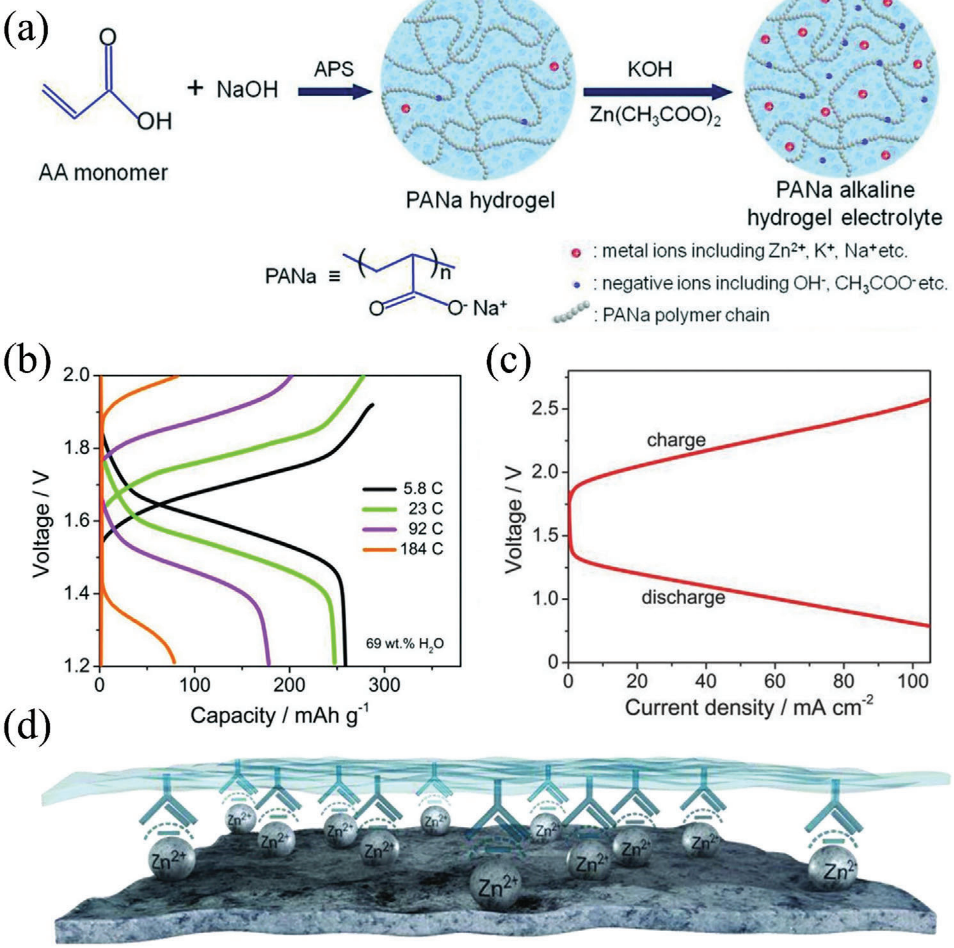


Figure 6. Hydrogel electrolyte for Zn anode. a) The PANa electrolyte obtained from the reactions of acrylic acid (AA monomer), NaOH (neutralizer), ammonium persulfate (APS, initiator), $Zn(CH_3COO)_2$, and KOH. Electrochemical performance of b) Zn||NiCo batteries and c) Zn–air batteries in this electrolyte. d) Schematic illustration showcasing the formation of quasi-SEI. Reproduced with permission.[61] Copyright 2018, Wiley-VCH.

infiltration of aqueous electrolyte turns into a hydrated state as a hydrogel, permitting the ion transport at the interface. The formed electrolyte-friendly interphase enables the uniform Zn deposition morphology.[60] In spite of the focus on applying the hydrogels in flexible devices, few efforts have been devoted to understanding the stabilization of hydrogel–solid interfaces on Zn electrode, which influences the reversibility of Zn deposition.

In 2018, a sodium polyacrylate-based hydrogel electrolyte (PANa) was reported for fabricating solid-state Zn batteries, in which both Zn||NiCo alkaline batteries and Zn–air batteries possessed high cycling stability and rate capabilities (**Figure 6**).[61] The high ionic conductivity and electrochemical stability of the electrolyte are responsible for the performance improvement, due to the highly hydrophilic nature of polymer networks efficiently anchoring the water molecules and anions. Besides, the strong interaction between the polymer backbone and Zn^{2+} promote the formation of a quasi-SEI layer on the Zn anode. This homogeneous quasi-SEI composed of characteristic C—O, C═O, and Zn—O species can facilitate the Zn metal nucleation, thus suppressing the Zn dendrite growth. Similarly, a zwitterionic sulfobetaine hydrogel electrolyte is also prepared by polymerizing natural sulfobetaine monomers and socked in a $ZnSO_4$ and $MnSO_4$ solution.[62] After cycling, the Zn electrode shows characteristic peaks of C═O, C—O, C—C, and Zn—O, confirming the existence of a polyzwitterion-facilitated quasi-SEI layer, which can significantly enhance the interface stability between the electrolyte and the electrode, contributing to the superior performance of the Zn anode. These results suggest that the superior performance of the Zn electrochemistry is mainly attributed to the quasi-SEI layer. However, the understanding of the interfacial chemistry in such hydrogel electrolytes, and the behavior of anions from the utilized salts at the interface remain unclear.

In a hydrogel system, the hydrogen bonded networks and solvation structures can be synergistically regulated in the presence of hydrophilic polymer frameworks. Meanwhile, the types of cations will also affect the phase transition behaviors (crystalline state) of hydrogels due to the change of the H-bonded structure, and consequently affect the properties of the electrolytes. In our previous work, a concentrated gel-type polymer electrolyte consisting of a hydrophilic poly(vinyl alcohol) polymer and an HCE (i.e., 21 m LiTFSI + 3 m Zn(OTf$_2$) was prepared for AZBs.[63] A transparent and stable hydrogel was obtained by use of a bication solution with high stability under subnormal temperatures and wide potential stability window. In this electrolyte, by-product and dendrite-free Zn stripping/plating performance was achieved. Accordingly, quasi-solid-state Zn||V_2O_5 batteries exhibited improved cycling stability and energy density. Moreover, the alginate-based polymer electrolytes were also proposed to constrain the water molecules in the aqueous electrolyte, which showed compatibility with the Zn anode with suppressed gas evolution, side reaction(s), and consequently achieving dendrite-free and smooth Zn deposition behaviors.[64] The use of biocompatible polymer in designing architectural polymer-state electrolyte is expanding green and sustainable strategies for the preparation of advanced polymer-based electrolyte for Zn batteries.

Anions in the hydrogel electrolyte also play a crucial role in affecting the anode performance. Using the dual-ion conducting polymer as frameworks in polymer electrolytes, anions tend to accumulate at the anode side and aggravate the concentration polarization issues, such as low efficiency, large voltage hysteresis, etc. In this respect, the anion mobility should be averted to the greatest extent during the design of Zn-based hydrogel electrolytes, which might be relieved by fixing anions to the polymer skeleton or combining anionic trapping agents. Also, a free volume design is also necessary at the interface for accommodating structural variation of electrodes and electrolyte.[65] To address these issues, grafting functional groups in the polymer frameworks, and optimizing salt concentration are expected to aid the design of advanced hydrogel electrolytes, which can decrease the reactivity of water, increase the mobility of Zn^{2+} by anchoring water molecules, and anions. Furthermore, the introduction of organic molecules is also a rational approach to overcome these obstacles for confining the anions.[66] For example, dimethyl sulfoxide (DMSO) with high donor number (DN) has been used to modify the hydrogel electrolyte, which tends to interact with the anions and promote the formation of an anion-derived SEI on the surface of substrates.[67] Even though, the high fabrication cost and low conductivity of polymer-based electrolytes and the inevitable electrode–electrolyte contact issues hinder their implementation in practical AZBs, which require high power, cost-efficiency, and long cycle life concerns.[57b,68]

Interestingly, the molecular crowding effect is a common phenomenon in living cells, in which the solution molecules can be modified when the macromolecules (such as proteins, complex sugars, polysaccharides) occur in the system.[69] In an aqueous solution, the reactivity of water molecules, for example, HER, can be well suppressed by taking advantage of the molecular crowding effect, which promotes the hydrogen-bonding interaction between water molecules and macromolecules.[70] Inspired by this phenomenon, designing molecular crowding aqueous electrolytes to reduce water activity can be efficient for suppressing water decomposition in aqueous batteries. Recently, a "molecular crowding" strategy by introducing polyethylene glycol (PEG400) as the H-bond donor into aqueous electrolyte was developed for aqueous LIBs, which can effectively decrease the water content and widen the stability window of the electrolyte.[71] As reported previously, the crowding environment can also change the solvation structure, and lower the plating exchange current density, hence enable the high reversibility of Zn metal electrode.[72]

In the standard molecular crowding electrolyte using the PEG (with a molecular weight of 400) as crowding agent, the reactivity of water, especially the hydrogen evolution reaction, can be significantly suppressed. To acquire further insights into the underlying mechanism, the cathodic stability of electrolytes using LiTFSI or $LiClO_4$ as salt was comparatively investigated.[74] The anion has a big impact on the cathodic stability. It is revealed that the composition of the SEI can affect the electrochemical stability of the electrolytes on the $Li_4Ti_5O_{12}$ electrode, and a robust LiF-rich SEI resulting from the decomposition of $TFSI^-$ anions contribute to the higher stability of the electrolyte with well-suppressed HER potential in molecular crowding electrolytes and enables the design of high-voltage aqueous LIBs. Moreover, the polyethylene glycol dimethyl ether 450 was also used as a new crowding agent for preparing aqueous molecular crowding electrolyte, displaying higher ionic conductivity (2.4 mS cm^{-1}) than that of the PEG400-based one (0.8 mS cm^{-1}) without sacrificing the voltage window (3.2 V).[75] Accordingly, a high-power and high-voltage aqueous $Li_4Ti_5O_{12}$||$LiMn_2O_4$ full-cell can be realized in this electrolyte (5 C, 72 Wh kg^{-1} vs 10 Wh kg^{-1} in PEG400) for 800 cycles. The formation of a stable LiF-rich SEI at relatively low LiTFSI concentration (2 m) was identified, which can be attributed to the decomposition of TFSI-anions. These results evidence the anion-derived SEI formation in hydrogel electrolytes and its prospective effect on improving electrode stability in aqueous batteries, which could be expanded to AZBs.

In AZBs, a strategy via adding PEG polymer network was also performed to engineer a diluted aqueous $Zn(OTf)_2$-based electrolyte, which can substantially reduce the water reactivity in the electrolyte, and high reversibility of Zn anode (**Figure 7**).[73] By constantly introducing PEG into the pristine electrolyte, the solvation structure of Zn^{2+} can be simultaneously regulated with more OTf^- and PEG present in the Zn^{2+} solvation sheath, which will greatly influence the local energy level of the electrolyte. The perturbation of the water hydrogen-bond network by H_2O-PEG interactions and anion-rich Zn^{2+} solvation sheath can facilitate the formation of a ZnF_2-rich SEI layer on the Zn anode. Based on this concept, a hydrophilic poly(ethylene glycol) methyl ether methacrylate polymer as a new type of crowding agent was introduced into the $Zn(OTf)_2$-based aqueous electrolyte, in which the hydrophilic molecular crowded polymer gel structure can reduce the free water molecules in electrolyte and inhibit the side reactions on Zn anode.[76] During the electrochemical operation, the ZnF_2 and ZnO species were detected on the anode, which could improve the Zn reversibility.

An aqueous electrolyte composed of 2 m $Zn(OTf)_2$ and 1 m NaOTf with 10 wt% PEG as a supporting polymer agent was designed, which efficiently suppresses the water activity and regulates the solvation structure of the cation, enabling highly reversible Zn plating/stripping.[77] Moreover, NASICON-type cathode $Na_3V_2(PO_4)_4$ (NVP) also demonstrates superior stability for Zn storage. An inorganic fluoride-rich SEI was observed on the cathode surface after cycling in the modified electrolyte, which acts as a robust and ionically conductive layer to prevent the NVP material from contact with aqueous electrolyte, thus contributing to a high-efficiency and stable Zn||NVP battery. The SEI can prevent dendrite growth on Zn anode and the structural deterioration of cathode material, leading to high cycling performance, safety and rate capability.

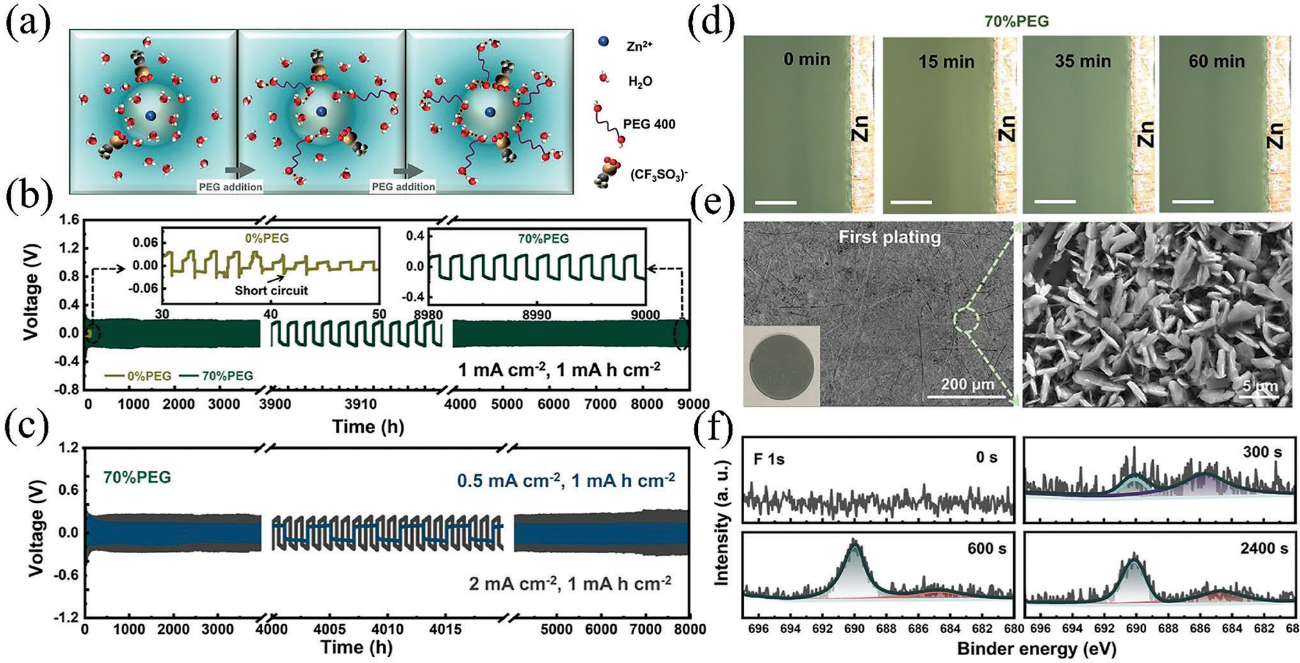


Figure 7. "Molecular crowding" electrolyte for Zn anode. a) Schematic illustration of the solvation structure change in the electrolytes with/without PEG as crowding agent. b) Galvanostatic cycling performance of the Zn||Zn symmetric cells. c) Galvanostatic cycling performance of the Zn||Zn cells in 70% PEG electrolyte at various current densities. d) In situ optical visualization observations of the Zn deposition behaviors in the modified electrolytes (scale bar: 200 µm). e) SEM images collected on the Zn anodes after first plating (inset is a photograph of the Zn anode). f) XPS characterization of SEI on the cycled Zn anodes. Reproduced with permission.[73] Copyright 2021, Elsevier.

3.4. Additive Strategy

Additive engineering has been demonstrated as an effective strategy to rationally regulate the solvation structure and corresponding interfacial chemistry in routine aqueous electrolytes, thus promoting the reversibility of Zn anode. Differing to the co-solvent strategy to form LHCEs, introducing a small amount of organic solvent molecules as additives into the aqueous electrolytes, which would preferentially coordinate with the Zn^{2+} cations due to the cation–solvent interactions, will affect the solvation structure of Zn^{2+} and thus enhances the performance of Zn anode.[78] Typically, the multifunctional fluoroethylene carbonate (FEC) has been introduced into an aqueous electrolyte as an organic additive to construct a high-quality and ZnF_2-rich SEI layer on the Zn metal anode surface.[79] The FEC can regulate the solvated structure of Zn^{2+} to reduce H_2O molecules' reactivity, while the hybrid SEI layer with strong Zn^{2+} affinity can avoid dendrite formation and direct contact between the electrolyte and the Zn anode. Hence, the dendrite growth, and side reactions (e.g., corrosion, HER, etc.) on the Zn anode are efficiently suppressed in FEC-containing $ZnSO_4$ aqueous electrolyte.[9b]

Although the organic molecule additive strategy can be effective in stabilizing the Zn anode, it remains unclear how the participation of coordinated organic solvents and anions in the Zn^{2+} solvation sheath, influence the intrinsic structure and properties of the SEI.[80] Recently, organic dimethyl carbonate (DMC) was used as additive in a dilute aqueous electrolyte, i.e., 2 m $Zn(OTf)_2$, and the as-proposed electrolytes were investigated for Zn anode.[81] It is observed that the introduction of DMC additive leads to changes in the Zn^{2+} solvation structure with quantifiable $Zn^{2+}[H_2O]_{3.9}[DMC]_{0.7}[OTf^-]_{1.4}$ complex, which is different to the typical $Zn[H_2O]_6{}^{2+}$ structure in 2 m $Zn(OTf)_2$). The coordinated DMC molecules and OTf^- anions contribute to the formation of SEI on Zn anode, in which the enrichment of $ZnCO_3$ and ZnF_2 components in the inner structure of SEI indicates the simultaneous decomposition of DMC and anion species. In the unique cation involved coordination structure, the DMC and OTf^- species become electrochemically unstable below 0.47 and 0.14 V (vs Zn^{2+}/Zn), respectively, and the electron could preferably transfer from the Zn^{2+} cation to the associated solvent and anion, thus facilitating their decomposition for the formation of anion/solvent-derived SEI at the electrode/electrolyte interface. Moreover, the highly polar organic solvent of propylene carbonate (PC) was also reported as cosolvent in the 1 m $Zn(OTf)_2$ aqueous electrolyte to improve the Zn plating/stripping reaction. The PC molecules participate in the solvation structure of Zn^{2+} due to the strong Zn^{2+}–PC interaction (**Figure 8**).[82] Such unique solvation structure change leads to the preferential reduction of anions before the solvents (water and PC), thus forming a hydrophobic SEI. Moreover, a highly stable and reversible anode-free Zn-based battery coupled with a $ZnMn_2O_4$ cathode and a Cu foil as anode current collector can be realized in this electrolyte (Figure 8g,h), benefiting from the highly reversible Zn anode and good compatibility with the intercalation cathode.[83]

The TEP organic molecule has been reported to contribute to the formation of a robust SEI for Zn batteries,[23] in which the solvent has also been used as additive to optimize the conventional aqueous electrolyte. Differing to the HEE system with much lower water content, an aqueous electrolyte with 0.5 m $Zn(OTf)_2$/TEP-H_2O formulation (in a TEP:H_2O volume ratio of

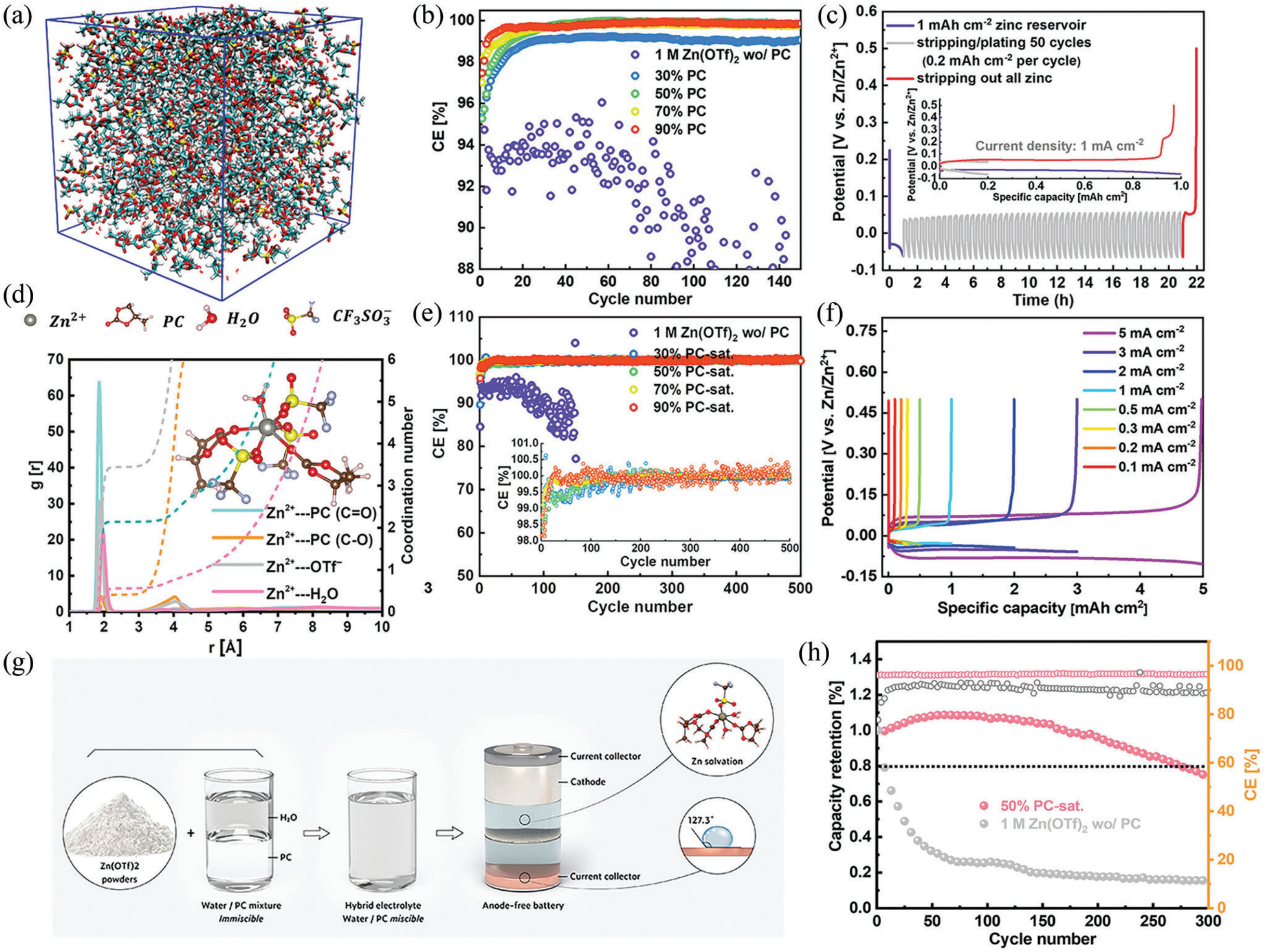


Figure 8. Organic molecule hybrid aqueous electrolyte for Zn anode. a) A snapshot of the MD simulation cell and b) corresponding RDF plots for electrolyte with PC as cosolvent. c,d) The CE of the Zn||Cu asymmetric cells upon long-term Zn plating/stripping test in various electrolytes. e) Voltage profiles of Zn||Cu cells in 50% PC-sat. hybrid electrolyte. f) Charge/discharge profiles of Zn||Cu asymmetric cells at various current densities. g) Schematic illustrations of the electrolyte, Zn solvation structure, and the as-fabricated anode-free cell configuration. h) Cycling performance of the anode-free Cu||ZnMn$_2$O$_4$ cells in different electrolytes. Reproduced with permission.[83] Copyright 2022, American Chemical Society.

1:1) was prepared and used for AZBs.[84] The strong coordination of TEP molecule with Zn^{2+} and H_2O promotes a TEP-dominated Zn^{2+} solvation sheath and inhibits the water reactivity, which significantly stabilizes the Zn anode and V_2O_5 cathode in the Zn||V_2O_5 full cell. Meanwhile, the TEP-involved solvation structure facilitates the formation of a robust polymeric-inorganic SEI layer, in which the polymetaphosphate is formed by the decomposition of TEP solvent and the inorganic components (i.e., ZnF_2, carbonates, and sulfate compounds) are produced by anion decomposition, effectively avoiding parasitic water reaction and dendrite growth on the Zn anode. As a result, the multifunctional hybrid electrolytes can not only support the formation of protective SEI layer on anode, but also introduce an ideal CEI layer that helps to improve the overall performance of AZBs. Despite this, the added organic molecules act similarly to the cosolvent, since a large portion was used in the solution. Nevertheless, these results suggest that modifying the cation–solvent interaction with additives in the solvation structure is a viable strategy to enhance the Zn anode's reversibility and the AZBs' cycling life.

Inspired by the LHCEs, the water reactivity and Zn^{2+} solvation structure in aqueous electrolyte can also be regulated through an antisolvent strategy, in which the antisolvent additives are miscible with water but less soluble with Zn salts. For example, in an aqueous $ZnSO_4$ electrolyte, the electrolyte structures were regulated by introducing methanol (DN = 19 kcal mol^{-1}) as a molecule-type additive. Methanol molecules can gradually interact with the free and coordinated water molecules in the electrolyte, which can weaken the Zn^{2+} solvation and reduce the water activity, leading to significantly inhibited side reactions and enhanced Zn^{2+} transference number. As a result, the Zn^{2+} deposition orientation was optimized, resulting in high reversibility of Zn anode.[85] Meanwhile, the weak coordination ability of antisolvent with Zn^{2+} can favor anion participation in the Zn^{2+} solvation sheath, and thus promote anion decomposition to form the anion-derived SEI. Theoretically, the antisolvent additive normally features a higher DN than H_2O (18 kcal mol^{-1}), preferring to form a free solvent molecule strongly hydrogen bonded with H_2O and forces the anions occupied in the inner solvation sheath around Zn^{2+}, which will alter the water reactivity and reductive stability of the anions. A small amount (2 vol%) of diethyl ether (Et_2O) (DN = 19.2 kcal mol^{-1}) as the molecule additive has been reported to largely improve the stability of aqueous Zn||MnO_2 batteries, benefitting from the efficiently suppressed formation of Zn dendrites during operation.[86] Similarly, the 1,2-dimethoxyethane (DME, DN = 20 kcal mol^{-1}) molecule additive was also used to simultaneously regulate the solvation structure in the aqueous electrolyte and corresponding interfacial chemistry on Zn anode.[87] Specifically, a hybrid electrolyte system was proposed by dissolving 2 m $Zn(OTf)_2$ into the H_2O/DME mixture solutions. The formulated electrolyte with 40 vol% DME possesses nonflammability and effectively stabilizes the Zn anode with an excellent cycling performance. The preferentially adsorbed DME molecules on the Zn surface and an in situ formed organic–inorganic OTf^--derived SEI layer can avoid the direct contact of Zn with water, prevent the Zn anode from dendrite formation, and homogenize Zn^{2+} plating. Thus, the introduction of molecule additive, e.g., organic solvents, will manipulate the solvation structure of Zn^{2+} and the hydrogen network with water, while a comprehensive understanding is still required to clarify the relationship between the anode performance and the nature of molecule additives. On the one hand, the interaction of additional molecules in the solvation structure will not only facilitate the anion-derived SEI formation, but also change the desolvation energy and hydrogen bonding network, which can affect the reactions at the interface. On the other hand, the presence of these organic molecules with different zincophilic ability can change the deposition behavior, inevitably determining the overall reversibility of Zn metal electrode.

Ionic materials are also a popular class of additives in the electrolyte engineering research field. Both inorganic and organic ionic additives in electrolyte can participate in the solvation structures of Zn^{2+}, and the structure and compositions of the SEI can be manipulated. There are specific literatures that discuss the role of inorganic ionic additives and metal ions in stabilizing the Zn anode in aqueous electrolytes.[88] It can be concluded that the ionic additives have a critical role in modifying the ionic conductivity, the stability window, the electric field distribution at the electrode surface, the side reactions related to the electrolyte species, etc., thus enhancing the electrochemical performance of Zn. To resolve the role of ionic additive on the formation of anion-induced SEI, a diluted aqueous electrolyte, i.e., 4 m $Zn(OTf)_2$ with 0.5 m trimethylethyl ammonium triflate ($Me_3EtNOTf$) as the ionic additive, was proposed by Wang and co-workers, which in situ generates a hydrophobic ZnF_2-rich layer derived from the anion decomposition and enables highly reversible Zn metal anode.[89] Trimethylamine resulting from the decomposition of alkylammonium cation works as catalyst to accelerate the conversion of OTf^- anions into the SEI. The cations from the additives can significantly affect the formation of the SEI layer, immediately initiating anion decomposition. Besides, the use of ionic additive will increase the ion concentration, and the anions would squeeze into the solvation sheath inducing the formation of an anion-based solvation structure. Such anion–cation–solvent complex provides the basis for anion reduction and the generation of anion-derived SEI.

In an attempt to regulate the solvation structure by introducing anionic additive, tetrasodium ethylenediaminetetraacetate (Na_4Y) was introduced into the 1 M $Zn(OTf)_2$ aqueous electrolyte to stabilize the Zn anodes, where a dual-anion-enrichment in Zn^{2+}-solvation sheath was formed.[90] The Y^{4-}-based solvation structure not only reduces the reactivity of water molecules but also leads to the homogeneous Zn^{2+} deposition reaction. A unique interphase layer on Zn is detected composed of an inorganic ZnF_2–ZnS-rich inner region and an organic-rich outer region, due to the decomposition of coordinated OTf^- anions. Moreover, an aqueous $Zn(OTf)_2$–$Zn(NO_3)_2$ electrolyte with low-concentration salts was prepared using the $Zn(NO_3)_2$ as the anionic additive without extra cations and applied in AZBs.[91] It was demonstrated that the self-terminated chemical reaction of NO_3^- anions with the existing Zn^{2+} and generated OH^- from HER induces the formation of an insulating $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ species on the Zn electrode, which will further transform into Zn-ion conducting $Zn_5(CO_3)_2(OH)_6$ electrochemically, as illustrated in **Figure 9**, and in turn promotes the formation of ZnF_2-rich structure in the inner SEI layer derived from the preferable reduction of OTf^-. The in situ anion-derived SEI enables a high energy density and long-term cycling stability of the fabricated Zn||MnO_2 full cells with a low N/P ratio of 2:1, owing to the improved Zn reversibility.

Besides facilitating the anion decomposition for the formation of SEI, the decomposition of the ionic additive also provides the opportunity to in situ form the SEI. A small amount of $Zn(H_2PO_4)_2$ salt (0.025 M) as the inorganic additive, was introduced into the 1 M $Zn(OTf)_2$ aqueous electrolyte, and the in situ formation of a Zn^{2+}-conductive SEI layer (hopeite, $Zn_3(PO_4)_2 \cdot 4H_2O$) was observed.[92] The dense and stable inorganic SEI with a thickness of ≈140 nm results from the decomposition of $H_2PO_4^-$ anions and substantial reaction with the Zn^{2+} cations. The presence of OH^- anions (stemming from HER) in the electrolyte facilitates the SEI generation. Consequently, the zinc phosphate-based SEI layer in situ formed on the Zn electrode ensures the high Zn utilization as anode, which further boosts the AZBs under practical testing conditions, such as at high areal capacity and high depth-of-discharge. Moreover, the PF_6^- anion-induced chemical strategy is also efficient to construct a Zn^{2+}-conductive but hydrophobic SEI by introducing the chemically reactive KPF_6 in 2 M $ZnSO_4$ aqueous electrolyte.[93] Specifically, PF_6^- is thermodynamically unstable in water and easily generates reactive acidic intermediate products such as POF_3, HF, and phosphoric acid species (HPO_2F_2, H_2PO_3F, and H_3PO_4), which will sequentially react with Zn^{2+} to form $Zn_3(PO_4)_2$ and ZnF_2 precipitations on the Zn anode, i.e., SEI, which can effectively suppress Zn dendrite growth and accelerate the kinetics of Zn^{2+} transport at the interface, thus resulting in enhanced reversibility of Zn anode.

Ionic liquids (ILs) are another class of promising ionic additives. The introduction of anions from the additive alters the solvation structures of Zn^{2+}, and the Zn plating behaviors can be controlled by adjusting the type of anions, which can be easily formulated in ILs. For example, the specific role of Cl^-, PF_6^-, $TFSI^-$, or DCA^- (dicyanamide) anions in imidazolium ILs has been examined in a 0.1 M $ZnSO_4$ and 1 M $(NH_4)_2SO_4$ electrolyte

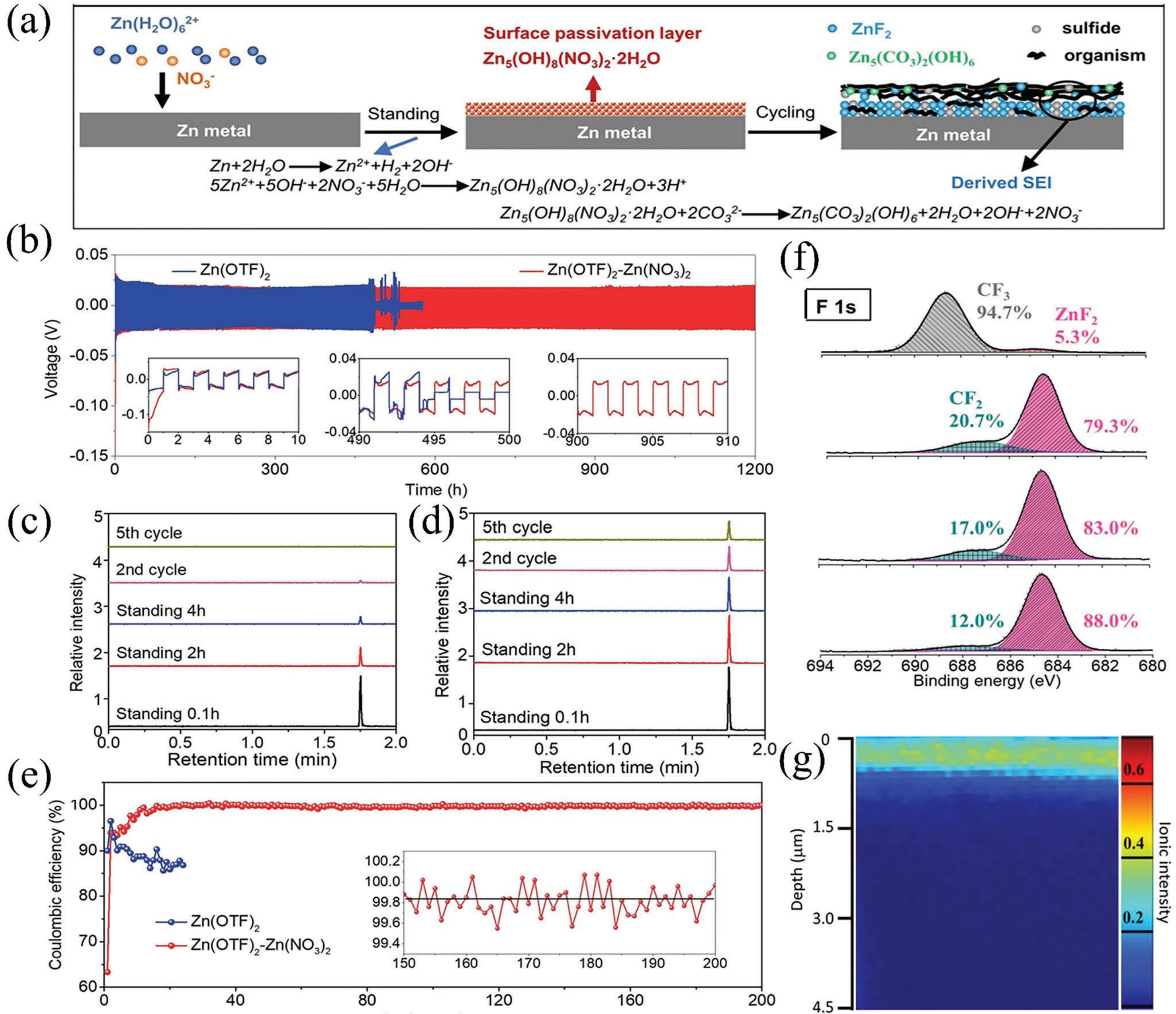


Figure 9. Anionic additive strategy in aqueous electrolyte for Zn anode. a) Formation mechanism of ZnF_2–$Zn_5(CO_3)_2(OH)_6$–organic SEI in the presence of NO_3^- anionic additive. b) Galvanostatic Zn plating/stripping in the Zn||Zn symmetrical cell at 0.5 mA cm^{-2} and 0.5 mAh cm^{-2}. Peak of hydrogen gas released from Zn||Zn cells using c) $Zn(OTf)_2$–$Zn(NO_3)_2$ and (d) $Zn(OTf)_2$ electrolytes before and after cycling. e) Zn plating/stripping CE in different electrolytes (inset: magnified view of Zn plating/stripping CE in $Zn(OTf)_2$–$Zn(NO_3)_2$ electrolyte). f) XPS F 1s peaks collected on the cycled Zn electrode within 0 s, 300 s, 900 s, and 1500 s Ar^+ sputtering. g) TOF-SIMS analysis for the F element. Reproduced with permission.[91] Copyright 2021, Wiley-VCH.

for Zn deposition, among which the addition of DCA^- anions is effective to inhibit the initiation and growth of dendritic Zn during plating.[94]

To examine the potential interfacial chemistry in the aqueous electrolyte with ionic liquid additive, the 1-butyl-3-methylimidazolium triflate ([BMIM]OTf), a miscible ionic liquid with water, was used as the example in a 3 M $Zn(OTf)_2$ aqueous electrolyte for AZBs.[96] As illustrated, the added $BMIM^+$ cations from the ionic liquid was preferentially adsorbed on the Zn anode, affecting the deposition behavior of Zn. Moreover, the OTf^- anions can participate in the solvation structure of Zn^{2+} and enable the formation of a cation/anion-derived hybrid SEI layer (rich in C–N, C–S, ZnF_2, $ZnSO_3$, and ZnS species). The presence of this SEI enables advanced aqueous batteries based on Zn metal electrochemistry, i.e., high energy densities and long cycling stabilities in Zn||$VOPO_4$, Zn||O_2, and Zn||MnO_2 full cells using limited Zn. A "water-in-ionic liquid" electrolyte composed of a ionic liquid mixture of[BMIM]TFSI/$Zn(TFSI)_2$ (in a molar ratio of 1:0.5) and 20 wt% water was developed for Zn anode (**Figure 10**).[95] With such ultrahigh ionic concentrations in the solution, the water molecules are surrounded by the anion-abundant frameworks, which construct unique channels for fast ionic conduction. Such formulation with limited free water molecules promotes the formation of a robust inorganic–organic complex SEI, originating from both the decomposition of BMI^+ cation and the reduction of $TFSI^-$ anions, contributing to an ex-

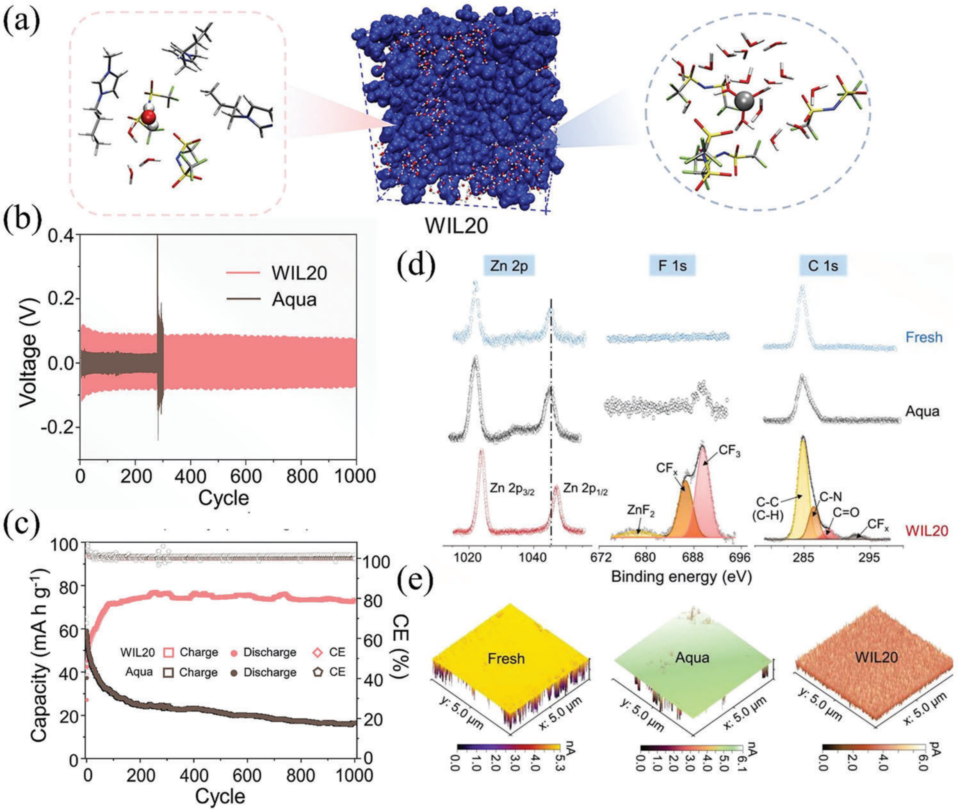


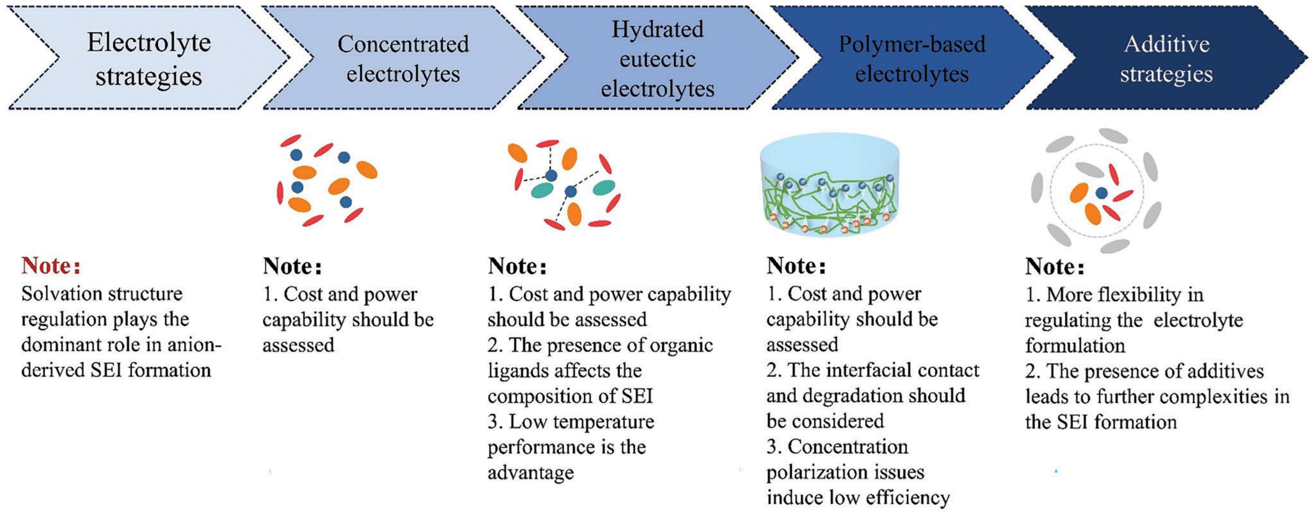
Figure 10. Cationic additive strategy in aqueous electrolyte for Zn anode. a) Snapshots from the MD simulation of an aqueous electrolyte with a mixture of BMIMTFSI/Zn(TFSI)$_2$ (in a molar ratio of 1:0.5) and 20 wt% water (denoted as WIL20). b) Long-term stripping/plating performance of Zn||Zn symmetric cell under conditions of 1 mA cm^{-2} and 0.5 mAh cm^{-2}. c) Cycling stability of the Zn||PANI full cells at 1000 mA g^{-1}. d) High-resolution Zn 2p, F 1s, and C 1s XPS peaks recorded on a fresh Zn anode, and cycled Zn anodes in different electrolytes. e) Current responses of a fresh Zn anode, and cycled Zn anodes in different electrolytes under DC sample bias of −1 V, obtained by AFM. Reproduced with permission.[95] Copyright 2022, American Chemical Society.

ceptionally reversible Zn electrochemistry. As a proof of concept, the as-fabricated Zn–air batteries in this electrolyte demonstrate superior long-term stability, ≈300 h versus 72 h compared to the batteries in routine aqueous electrolyte. In our recent work, the addition of foreign anions with competitive solvation capability, i.e., stronger interaction with cations, was adopted to promote the anion-enriched solvation structure.[97] The sustainable IL as additive, i.e., methylammonium acetate, enables the byproduct-free and dendrite-free Zn stripping/plating reactions over long-term cycling, and the OTf$^-$ anion-derived SEI with ZnS/ZnF$_2$ heterostructure was disclosed, illustrating the superior performance of Zn achieved in dilute aqueous electrolyte. Both battery (NVP as positive electrode) and capacitor (activated carbon as positive electrode) demonstrated much improved cycling stability based on the Zn electrochemistry. These results provide an efficient way to rationally design the composition and structure of in situ formed SEI for Zn metal electrochemistry by changing the competitive anion types in the solvation structure.

With the additive strategy, more complex mechanisms generate and influence the SEI formation, composition and structure due to the inclusion of additive anions which electrochemically decompose. However, in contrast to the artificial interphase strategy, the simplicity of this approach showcases the potential for implementation in practical applications, which addresses the concerns regarding the difficulty of efficient SEI formation in a conventional aqueous electrolyte. Although these manipulations of the electrolyte have shown a positive effect on improving the reversibility of Zn anode, the underlying mechanisms have yet to be entirely understood. Moreover, the water reactivity, Zn^{2+} flux, desolvation energy, and other parameters should also be considered as key factors impacting the performance.

4. Summary and Perspectives

In conclusion, this review summarizes the recent achievements of electrolyte engineering to facilitate the anion-derived SEI chemistries. The mechanisms and challenges are summarized in **Figure 11**. It has been proven that the robust SEI formation dominated by the anion decomposition in aqueous electrolyte plays a significant role in enhancing the reversibility of Zn anode, associated with the modulated electron conduction and ion transport behavior at the electrode/electrolyte interface. Consequently, the dendrite formation, side reaction, passivation, and morphology evolution of Zn metal operating in aqueous electrolytes can be efficiently inhibited in the presence of the robust SEI layer. To facilitate the in situ anion-derived SEI formation, pa-



Note:
Solvation structure regulation plays the dominant role in anion-derived SEI formation

Note:
1. Cost and power capability should be assessed

Note:
1. Cost and power capability should be assessed
2. The presence of organic ligands affects the composition of SEI
3. Low temperature performance is the advantage

Note:
1. Cost and power capability should be assessed
2. The interfacial contact and degradation should be considered
3. Concentration polarization issues induce low efficiency

Note:
1. More flexibility in regulating the electrolyte formulation
2. The presence of additives leads to further complexities in the SEI formation

Figure 11. Summary of the emerging strategies for facilitating the anion-derived SEI.

rameters including the salt concentration, and electrolyte formulation can be manipulated in the electrolytes, which will reduce the water activity and change the compositions in the Zn^{2+} solvation shell. The conventional electrolyte chemistries of (localized) HCEs, HEEs, hydrogel electrolytes, and MCEs, are discussed, in which the formation of anion-based solvation structure is beneficial for the formation of the anion-derived SEI. Attempts have also been made to enhance the performance of Zn anode using additives. The introduction of molecule and ionic additives leads to further complexities in the SEI formation apart from the known "anion-solvation-strategy" since the decomposition of additives affect the formation mechanism and compositions of SEI.

Even though, the fundamental understanding of the interfacial chemistries related to the anions in the aqueous electrolytes is still insufficient, the SEI has a great influence on the ion migration from the electrolyte to electrode, where the desolvation occurs as the rate-limiting step at the interface. Uniform and robust SEI could protect the inevitable decomposition of electrolyte and prevent the electrodes from the parasitic reactions related to water. However, the structure and composition of SEI are still difficult to regulate by anion-derived interfacial chemistry in aqueous systems. Moreover, the SEI is usually formed unevenly and can be destroyed by the stress caused by the electrode volume changes upon cycling. Despite the current progress, critical challenges still remain. In particular, due to the complexity of the SEI formation process in aqueous electrolytes, further efforts on the fundamental understanding of working and failure mechanisms of SEI in aqueous systems are requisite to improve the zinc electrode performance. Some perspectives and key factors to promote the interphasial chemistry in AZBs are presented as follows.

1) Further understanding of the interfacial chemistry. In aqueous electrolytes, the anion-based interfacial reaction products are more complex, and the electron conduction and ion transport mechanisms, solvation and desolvation behaviors of Zn^{2+} at the Zn metal|SEI|electrolyte interfaces, and the degradation mechanisms of SEI need to be fully understood. Although the postmortem characterizations based on X-ray techniques have been widely adopted to detect the compositions of electrodes and their surface after cycling, in situ/operando methods to dynamically monitor interfacial reactions between electrolyte and electrode remain difficult to evaluate to satisfy the requirements for practical applications. In situ observation techniques during electrochemical analysis (e.g., cryogenic electron microscopy, Raman microscopy, etc.) can be used to track the evolutions of structure and detect the changes of compositions of Zn electrodes and aqueous electrolytes during the continuous dissolution and deposition processes. Moreover, predictive modeling and theoretical calculations at the molecular/electronic level are of relevance to understand and resolve the interfacial reactions at the nanoscale.
2) Accurate construction of SEI models and identifying their roles in improving the performance. It has been widely recognized that the multilayer architecture of SEI in organic electrolytes strongly affects the stability of metal electrodes (such as Li, Na, and K), while the specific components in the SEI within the aqueous electrolytes still remain unclear. The anion-derived interfacial chemistry provides the possibility for the rational design of the architecture and compositions in the SEI; each specific species and structure should be connected to the performance metrics.
3) Further development of advanced strategies facilitating the formation of anion-derived SEI should be explored. Although current progress has significantly improved the reversibility of Zn anode by electrolyte optimization, advanced strategies with simplified fabrication and cost-efficiency are still required. The recent exploration of hydrogel electrolytes suggests that the suppressed water-reactivity and modulated anion-rich solvation structures can be beneficial for SEI formation. Besides the anions, solvents in the electrolytes can also contribute to the formation of a functional SEI. As a proof-of-concept, dimethyl methylphosphonate and DMSO solvents are viable candidates for the formation of solvent-derived SEI, resulting from the decomposition of solvated organic molecules.[98] Also, the design of semisolid aqueous

electrolytes with suppressed water reactivity may stabilize the interface and promote the rechargeability of AZBs.

4) The anion-derived CEI should also be considered. Although the strategy and formation of SEI on the Zn anode has been emphasized, the understanding of anion contribution for CEI formation is not adequate. For example, the addition of PC solvent in the routine aqueous electrolyte will also form the localized high-concentration structure at the cathode–electrolyte interface, which can prevent the $NaV_3O_8 \cdot 1.5H_2O$ cathode material from contacting H_2O.[99] In this respect, due to the variety of cathode materials and their complex reaction mechanisms, the interfacial chemistry on the cathodes and their Zn^{2+} transport/storage kinetics need to be extensively clarified and optimized, which will further strengthen the overall performance of AZBs.
5) Electrolyte design should be integrated for practical batteries. Although the electrolyte-derived interfacial chemistry is essential for the successful operation of current commercial Li-ion battery systems, however, for aqueous batteries, the performance is always evaluated in lab-scale cells. The low Zn loading limits the depth of discharge and is far from the actual operating conditions. Therefore, it is necessary to assess the electrolytes and their interphasial chemistry with high proportion Zn electrode under more practical conditions. Moreover, to boost the AZBs for practical applications, standard assessment methods should be established to evaluate specific energy/power densities, and cost, which will aid the facile determination of feasible electrolytes.

In conclusion, future studies of the anion-derived interfacial chemistry in the AZBs will resolve the reversibility issues of Zn anode and promote the performance enhancement of aqueous energy storage technologies based on Zn metal electrochemistry.

Acknowledgements

This work was financially supported by the Natural Science Foundation of China (Grant No. 52277215), the Natural Science Foundation of Chongqing (cstc2020jcyj-msxmX0667), and the Fundamental Research Funds for the Central Universities, and the Helmholtz Association within the Network of Excellence on post-Lithium batteries (ExNet-0035). H.A. acknowledges the support of the University of Hong Kong and the Hong Kong Quantum AI Lab Limited, AIR@InnoHK.

Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

aqueous electrolytes, reversibility, SEI, solvation structure, Zn anodes

Received: April 27, 2023
Revised: June 20, 2023
Published online:

---

[1] a) B. Dunn, H. Kamath, J.-M. Tarascon, *Science* **2011**, *334*, 928; b) N. Kittner, F. Lill, D. M. Kammen, *Nat. Energy* **2017**, *2*, 17125.
[2] J. O. G. Posada, A. J. R. Rennie, S. P. Villar, V. L. Martins, J. Marinaccio, A. Barnes, C. F. Glover, D. A. Worsley, P. J. Hall, *Renewable Sustainable Energy Rev.* **2017**, *68*, 1174.
[3] a) L. E. Blanc, D. Kundu, L. F. Nazar, *Joule* **2020**, *4*, 771; b) C. Li, S. Jin, L. A. Archer, L. F. Nazar, *Joule* **2022**, *6*, 1733.
[4] a) L. Hu, P. Xiao, L. Xue, H. Li, T. Zhai, *Chem* **2021**, *3*, 100052; b) F. Wan, X. Zhou, Y. Lu, Z. Niu, J. Chen, *ACS Energy Lett.* **2020**, *5*, 3569.
[5] M. Chen, S. Xie, X. Zhao, W. Zhou, Y. Li, J. Zhang, Z. Chen, D. Chao, *Energy Storage Mater.* **2022**, *51*, 683.
[6] a) Y. Liu, S. Liu, X. Xie, Z. Li, P. Wang, B. Lu, S. Liang, Y. Tang, J. Zhou, *InfoMat* **2023**, *5*, 12374; b) Y. Song, P. Ruan, C. Mao, Y. Chang, L. Wang, L. Dai, P. Zhou, B. Lu, J. Zhou, Z. He, *Nano-Micro Lett.* **2022**, *14*, 218; c) W. Nie, H. Cheng, Q. Sun, S. Liang, X. Lu, B. Lu, J. Zhou, *Small Methods* 2201572, https://doi.org/10.1002/smtd.202201572.
[7] a) M. Gauthier, T. J. Carney, A. Grimaud, L. Giordano, N. Pour, H.-H. Chang, D. P. Fenning, S. F. Lux, O. Paschos, C. Bauer, F. Maglia, S. Lupart, P. Lamp, Y. Shao-Horn, *J. Phys. Chem. Lett.* **2015**, *6*, 4653; b) Y. Xiao, Y. Wang, S.-H. Bo, J. C. Kim, L. J. Miara, G. Ceder, *Nat. Rev. Mater.* **2020**, *5*, 105.
[8] E. Peled, *J. Electrochem. Soc.* **1979**, *126*, 2047.
[9] a) K. Xu, *Chem. Rev.* **2014**, *114*, 11503; b) H. Zhang, L. Qiao, H. Kühnle, E. Figgemeier, M. Armand, G. G. Eshetu, *Energy Environ. Sci.* **2023**, *16*, 11.
[10] J. B. Goodenough, Y. Kim, *Chem. Mater.* **2010**, *22*, 587.
[11] a) L. Suo, D. Oh, Y. Lin, Z. Zhuo, O. Borodin, T. Gao, F. Wang, A. Kushima, Z. Wang, H.-C. Kim, Y. Qi, W. Yang, F. Pan, J. Li, K. Xu, C. Wang, *J. Am. Chem. Soc.* **2017**, *139*, 18670; b) H. Zhang, X. Liu, H. Li, I. Hasa, S. Passerini, *Angew. Chem., Int. Ed.* **2021**, *60*, 598.
[12] S. Ko, Y. Yamada, A. Yamada, *ACS Appl. Mater. Interfaces* **2019**, *11*, 45554.
[13] a) X. Wang, X. Li, H. Fan, L. Ma, *Nano-Micro Lett.* **2022**, *14*, 205; b) P. Xiong, Y. Zhang, J. Zhang, S. H. Baek, L. Zeng, Y. Yao, H. S. Park, *Chem* **2022**, *4*, 100076.
[14] L. Yuan, J. Hao, C.-C. Kao, C. Wu, H.-K. Liu, S.-X. Dou, S.-Z. Qiao, *Energy Environ. Sci.* **2021**, *14*, 5669.
[15] a) Q. Zhao, S. Stalin, L. A. Archer, *Joule* **2021**, *5*, 1119; b) L. Ma, M. A. Schroeder, O. Borodin, T. P. Pollard, M. S. Ding, C. Wang, K. Xu, *Nat. Energy* **2020**, *5*, 743.
[16] a) W. Lu, C. Zhang, H. Zhang, X. Li, *ACS Energy Lett.* **2021**, *6*, 2765; b) J. Wang, Y. Yang, Y. Zhang, Y. Li, R. Sun, Z. Wang, H. Wang, *Energy Storage Mater.* **2021**, *35*, 19.
[17] Z. Cao, P. Zhuang, X. Zhang, M. Ye, J. Shen, P. M. Ajayan, *Adv. Energy Mater.* **2020**, *10*, 2001599.
[18] W. Hu, J. Ju, N. Deng, M. Liu, W. Liu, Y. Zhang, L. Fan, W. Kang, B. Cheng, *J. Mater. Chem. A* **2021**, *9*, 25750.
[19] E. Peled, S. Menkin, *J. Electrochem. Soc.* **2017**, *164*, A1703.
[20] a) J. Han, H. Euchner, M. Kuenzel, S. M. Hosseini, A. Groß, A. Varzi, S. Passerini, *ACS Energy Lett.* **2021**, *6*, 3063; b) J. Hao, B. Li, X. Li, X. Zeng, S. Zhang, F. Yang, S. Liu, D. Li, C. Wu, Z. Guo, *Adv. Mater.* **2020**, *32*, 2003021.
[21] T. Wang, P. Wang, L. Pan, Z. He, L. Dai, L. Wang, S. Liu, S. C. Jun, B. Lu, S. Liang, J. Zhou, *Adv. Energy Mater.* **2023**, *13*, 2203523.
[22] C. Mao, Y. Chang, X. Zhao, X. Dong, Y. Geng, N. Zhang, L. Dai, X. Wu, L. Wang, Z. He, *J. Energy Chem.* **2022**, *75*, 135.
[23] S. Di, X. Nie, G. Ma, W. Yuan, Y. Wang, Y. Liu, S. Shen, N. Zhang, *Energy Storage Mater.* **2021**, *43*, 375.
[24] a) H. Sonoki, M. Matsui, N. Imanishi, *J. Electrochem. Soc.* **2019**, *166*, A3593; b) T. Li, X.-Q. Zhang, N. Yao, Y.-X. Yao, L.-P. Hou, X. Chen, M.-Y. Zhou, J.-Q. Huang, Q. Zhang, *Angew. Chem., Int. Ed.* **2021**, *60*, 22683; c) Y. Xiao, R. Xu, L. Xu, J.-F. Ding, J.-Q. Huang, *Energy Mater.* **2021**, *1*, 100013.
[25] C. Yan, R. Xu, Y. Xiao, J.-F. Ding, L. Xu, B.-Q. Li, J.-Q. Huang, *Adv. Funct. Mater.* **2020**, *30*, 1909887.
[26] G. Park, K. Lee, D.-J. Yoo, J. W. Choi, *ACS Energy Lett.* **2022**, *7*, 4274.

[27] L. Zhou, S. Tian, X. Du, T. Liu, H. Zhang, J. Zhang, S. Hu, Z. Chen, J. Zhang, G. Cui, *ACS Energy Lett.* **2023**, *8*, 40.

[28] Y.-X. Yao, X. Chen, C. Yan, X.-Q. Zhang, W.-L. Cai, J.-Q. Huang, Q. Zhang, *Angew. Chem., Int. Ed.* **2021**, *60*, 4090.

[29] C. Yan, L.-L. Jiang, Y.-X. Yao, Y. Lu, J.-Q. Huang, Q. Zhang, *Angew. Chem., Int. Ed.* **2021**, *60*, 8521.

[30] J. Hu, Y. Ji, G. Zheng, W. Huang, Y. Lin, L. Yang, F. Pan, *Aggregate* **2022**, *3*, 153.

[31] L. Suo, O. Borodin, T. Gao, M. Olguin, J. Ho, X. Fan, C. Luo, C. Wang, K. Xu, *Science* **2015**, *350*, 938.

[32] a) J. Zheng, J. A. Lochala, A. Kwok, Z. D. Deng, J. Xiao, *Adv. Sci.* **2017**, *4*, 1700032; b) Y. Yamada, J. Wang, S. Ko, E. Watanabe, A. Yamada, *Nat. Energy* **2019**, *4*, 269.

[33] G. A. Giffin, *Nat. Commun.* **2022**, *13*, 5250.

[34] Y. Zhu, J. Yin, X. Zheng, A.-H. Emwas, Y. Lei, O. F. Mohammed, Y. Cui, H. N. Alshareef, *Energy Environ. Sci.* **2021**, *14*, 4463.

[35] F. Wang, O. Borodin, T. Gao, X. Fan, W. Sun, F. Han, A. Faraone, J. A. Dura, K. Xu, C. Wang, *Nat. Mater.* **2018**, *17*, 543.

[36] A. Clarisza, H. K. Bezabh, S.-K. Jiang, C.-J. Huang, B. W. Olbasa, S.-H. Wu, W.-N. Su, B. J. Hwang, *ACS Appl. Mater. Interfaces* **2022**, *14*, 36644.

[37] X. Xu, H. Su, J. Zhang, Y. Zhong, Y. Xu, Z. Qiu, H. B. Wu, X. Wang, C. Gu, J. Tu, *ACS Energy Lett.* **2022**, *7*, 4459.

[38] Y. Huang, W. Sun, K. Xu, J. Zhang, H. Zhang, J. Li, L. He, L. Cai, F. Fu, J. Qin, H. Chen, *Energy Storage Mater.* **2022**, *46*, 577.

[39] S. Chen, Q. Nian, L. Zheng, B.-Q. Xiong, Z. Wang, Y. Shen, X. Ren, *J. Mater. Chem. A* **2021**, *9*, 22347.

[40] S. P. Beltran, X. Cao, J.-G. Zhang, P. Z. El-Khoury, P. B. Balbuena, *J. Mater. Chem. A* **2021**, *9*, 17459.

[41] N. Wang, Y. Yang, X. Qiu, X. Dong, Y. Wang, Y. Xia, *ChemSusChem* **2020**, *13*, 5556.

[42] R. Xiao, Z. Cai, R. Zhan, J. Wang, Y. Ou, Z. Yuan, L. Wang, Z. Lu, Y. Sun, *Chem. Eng. J.* **2021**, *420*, 129642.

[43] Z. Miao, F. Zhang, H. Zhao, M. Du, H. Li, H. Jiang, W. Li, Y. Sang, H. Liu, S. Wang, *Adv. Funct. Mater.* **2022**, *32*, 2111635.

[44] E. L. Smith, A. P. Abbott, K. S. Ryder, *Chem. Rev.* **2014**, *114*, 11060.

[45] a) C. Zhang, L. Zhang, Y. Ding, X. Guo, G. Yu, *ACS Energy Lett.* **2018**, *3*, 2875; b) C. Zhang, L. Zhang, G. Yu, *Acc. Chem. Res.* **2020**, *53*, 1648.

[46] X. Lu, E. J. Hansen, G. He, J. Liu, *Small* **2022**, *18*, 2200550.

[47] M. Han, J. Huang, X. Xie, T. C. Li, J. Huang, S. Liang, J. Zhou, H. J. Fan, *Adv. Funct. Mater.* **2022**, *32*, 2110957.

[48] a) X. Lin, G. Zhou, M. J. Robson, J. Yu, S. C. T. Kwok, F. Ciucci, *Adv. Funct. Mater.* **2022**, *32*, 2109322; b) Y. Zhu, X. Guo, Y. Lei, W. Wang, A.-H. Emwas, Y. Yuan, Y. He, H. N. Alshareef, *Energy Environ. Sci.* **2022**, *15*, 1282.

[49] a) Q. Zhang, Y. Ma, Y. Lu, L. Li, F. Wan, K. Zhang, J. Chen, *Nat. Commun.* **2020**, *11*, 4463; b) Q. Zhang, K. Xia, Y. Ma, Y. Lu, L. Li, J. Liang, S. Chou, J. Chen, *ACS Energy Lett.* **2021**, *6*, 2704.

[50] J. Shi, T. Sun, J. Bao, S. Zheng, H. Du, L. Li, X. Yuan, T. Ma, Z. Tao, *Adv. Funct. Mater.* **2021**, *31*, 2102035.

[51] W. Yang, X. Du, J. Zhao, Z. Chen, J. Li, J. Xie, Y. Zhang, Z. Cui, Q. Kong, Z. Zhao, C. Wang, Q. Zhang, G. Cui, *Joule* **2020**, *4*, 1557.

[52] D. Han, C. Cui, K. Zhang, Z. Wang, J. Gao, Y. Guo, Z. Zhang, S. Wu, L. Yin, Z. Weng, F. Kang, Q.-H. Yang, *Nat. Sustainability* **2022**, *5*, 205.

[53] T.-Y. Chen, T.-J. Lin, B. Vedhanarayanan, H.-H. Shen, T.-W. Lin, *J. Colloid Interface Sci.* **2023**, *629*, 166.

[54] G. Ma, S. Di, Y. Wang, W. Yuan, X. Ji, K. Qiu, M. Liu, X. Nie, N. Zhang, *Energy Storage Mater.* **2023**, *54*, 276.

[55] H. Qiu, X. Du, J. Zhao, Y. Wang, J. Ju, Z. Chen, Z. Hu, D. Yan, X. Zhou, G. Cui, *Nat. Commun.* **2019**, *10*, 5374.

[56] Q. Yang, G. Liang, Y. Guo, Z. Liu, B. Yan, D. Wang, Z. Huang, X. Li, J. Fan, C. Zhi, *Adv. Mater.* **2019**, *31*, 1903778.

[57] a) P. Zhang, K. Wang, P. Pei, Y. Zuo, M. Wei, X. Liu, Y. Xiao, J. Xiong, *Mater. Today Chem.* **2021**, *21*, 100538; b) R. Ma, Z. Xu, X. Wang, *Energy Environ. Mater.* 12464, https://doi.org/10.1002/eem2.12464.

[58] J. Cong, X. Shen, Z. Wen, X. Wang, L. Peng, J. Zeng, J. Zhao, *Energy Storage Mater.* **2021**, *35*, 586.

[59] a) J.-L. Yang, J. Li, J.-W. Zhao, K. Liu, P. Yang, H. J. Fan, *Adv. Mater.* **2022**, *34*, 2202382; b) S. Wu, M. Hua, Y. Alsaid, Y. Du, Y. Ma, Y. Zhao, C.-Y. Lo, C. Wang, D. Wu, B. Yao, J. Strzalka, H. Zhou, X. Zhu, X. He, *Adv. Mater.* **2021**, *33*, 2007829.

[60] J. Shin, J. Lee, Y. Kim, Y. Park, M. Kim, J. W. Choi, *Adv. Energy Mater.* **2021**, *11*, 2100676.

[61] Y. Huang, Z. Li, Z. Pei, Z. Liu, H. Li, M. Zhu, J. Fan, Q. Dai, M. Zhang, L. Dai, C. Zhi, *Adv. Energy Mater.* **2018**, *8*, 1802288.

[62] F. Mo, Z. Chen, G. Liang, D. Wang, Y. Zhao, H. Li, B. Dong, C. Zhi, *Adv. Energy Mater.* **2020**, *10*, 2000035.

[63] H. Zhang, X. Liu, H. Li, B. Qin, S. Passerini, *ACS Appl. Mater. Interfaces* **2020**, *12*, 15305.

[64] a) C. Li, X. Xie, H. Liu, P. Wang, C. Deng, B. Lu, J. Zhou, S. Liang, *Natl. Sci. Rev.* **2022**, *9*, 177; b) X. Xie, J. Li, Z. Xing, B. Lu, S. Liang, J. Zhou, *Natl. Sci. Rev.* **2023**, *10*, 281.

[65] K. Wu, J. Huang, J. Yi, X. Liu, Y. Liu, Y. Wang, J. Zhang, Y. Xia, *Adv. Energy Mater.* **2020**, *10*, 1903977.

[66] S. Lee, J. Hwang, W.-J. Song, S. Park, *Batteries Supercaps* **2022**, *5*, 202200237.

[67] L. Wang, K. Uosaki, H. Noguchi, *J. Phys. Chem. C* **2020**, *124*, 12381.

[68] M. Han, T. C. Li, D.-S. Li, H. Y. Yang, *Batteries Supercaps* **2023**, *6*, 202200560.

[69] a) S.-i. Nakano, D. Miyoshi, N. Sugimoto, *Chem. Rev.* **2014**, *114*, 2733; b) D. Kilburn, J. H. Roh, L. Guo, R. M. Briber, S. A. Woodson, *J. Am. Chem. Soc.* **2010**, *132*, 8690.

[70] Y. Guo, J. Gu, R. Zhang, S. Zhang, Z. Li, Y. Zhao, Z. Huang, J. Fan, Z. Chen, C. Zhi, *Adv. Energy Mater.* **2021**, *11*, 2101699.

[71] J. Xie, Z. Liang, Y.-C. Lu, *Nat. Mater.* **2020**, *19*, 1006.

[72] S. J. Banik, R. Akolkar, *J. Electrochem. Soc.* **2013**, *160*, D519.

[73] Y. Wu, Z. Zhu, D. Shen, L. Chen, T. Song, T. Kang, Z. Tong, Y. Tang, H. Wang, C. S. Lee, *Energy Storage Mater.* **2022**, *45*, 1084.

[74] J. Xie, Y. Guan, Y. Huang, Y.-C. Lu, *Chem. Mater.* **2022**, *34*, 5176.

[75] D. Dong, J. Xie, Z. Liang, Y.-C. Lu, *ACS Energy Lett.* **2022**, *7*, 123.

[76] P. Samanta, S. Ghosh, H. Kolya, C.-W. Kang, N. C. Murmu, T. Kuila, *ACS Appl. Mater. Interfaces* **2022**, *14*, 1138.

[77] G. Guo, X. Tan, K. Wang, H. Zhang, *ChemSusChem* **2022**, *15*, 202200313.

[78] D. Wang, Q. Li, Y. Zhao, H. Hong, H. Li, Z. Huang, G. Liang, Q. Yang, C. Zhi, *Adv. Energy Mater.* **2022**, *12*, 2102707.

[79] D. Xie, Y. Sang, D.-H. Wang, W.-Y. Diao, F.-Y. Tao, C. Liu, J.-W. Wang, H.-Z. Sun, J.-P. Zhang, X.-L. Wu, *Angew. Chem., Int. Ed.* **2023**, *62*, 202216934.

[80] R. Meng, H. Li, Z. Lu, C. Zhang, Z. Wang, Y. Liu, W. Wang, G. Ling, F. Kang, Q.-H. Yang, *Adv. Mater.* **2022**, *34*, 2200677.

[81] Y. Dong, L. Miao, G. Ma, S. Di, Y. Wang, L. Wang, J. Xu, N. Zhang, *Chem. Sci.* **2021**, *12*, 5843.

[82] B. Kakoty, R. Vengarathody, S. Mukherji, V. Ahuja, A. Joseph, C. Narayana, S. Balasubramanian, P. Senguttuvan, *J. Mater. Chem. A* **2022**, *10*, 12597.

[83] F. Ming, Y. Zhu, G. Huang, A.-H. Emwas, H. Liang, Y. Cui, H. N. Alshareef, *J. Am. Chem. Soc.* **2022**, *144*, 7160.

[84] S. Liu, J. Mao, W. K. Pang, J. Vongsvivut, X. Zeng, L. Thomsen, Y. Wang, J. Liu, D. Li, Z. Guo, *Adv. Funct. Mater.* **2021**, *31*, 2104281.

[85] J. Hao, L. Yuan, C. Ye, D. Chao, K. Davey, Z. Guo, S.-Z. Qiao, *Angew. Chem., Int. Ed.* **2021**, *60*, 7366.

[86] W. Xu, K. Zhao, W. Huo, Y. Wang, G. Yao, X. Gu, H. Cheng, L. Mai, C. Hu, X. Wang, *Nano Energy* **2019**, *62*, 275.

[87] G. Ma, L. Miao, Y. Dong, W. Yuan, X. Nie, S. Di, Y. Wang, L. Wang, N. Zhang, *Energy Storage Mater.* **2022**, *47*, 203.

[88] a) S. Guo, L. Qin, T. Zhang, M. Zhou, J. Zhou, G. Fang, S. Liang, *Energy Storage Mater.* **2021**, *34*, 545; b) Y. Du, Y. Li, B. B. Xu, T. X. Liu, X. Liu, F. Ma, X. Gu, C. Lai, *Small* **2022**, *18*, 2104640; c) X. Wang, C. Han, S. Dou, W. Li, *Nano Mater. Sci.* **2022**, https://doi.org/10.1016/j.nanoms.2022.10.004.
[89] L. Cao, D. Li, T. Pollard, T. Deng, B. Zhang, C. Yang, L. Chen, J. Vatamanu, E. Hu, M. J. Hourwitz, L. Ma, M. Ding, Q. Li, S. Hou, K. Gaskell, J. T. Fourkas, X.-Q. Yang, K. Xu, O. Borodin, C. Wang, *Nat. Nanotechnol.* **2021**, *16*, 902.
[90] S. Di, L. Miao, Y. Wang, G. Ma, Y. Wang, W. Yuan, K. Qiu, X. Nie, N. Zhang, *J. Power Sources* **2022**, *535*, 231452.
[91] D. Li, L. Cao, T. Deng, S. Liu, C. Wang, *Angew. Chem., Int. Ed.* **2021**, *60*, 13035.
[92] X. Zeng, J. Mao, J. Hao, J. Liu, S. Liu, Z. Wang, Y. Wang, S. Zhang, T. Zheng, J. Liu, P. Rao, Z. Guo, *Adv. Mater.* **2021**, *33*, 2007416.
[93] Y. Chu, S. Zhang, S. Wu, Z. Hu, G. Cui, J. Luo, *Energy Environ. Sci.* **2021**, *14*, 3609.
[94] Y. Song, J. Hu, J. Tang, W. Gu, L. He, X. Ji, *ACS Appl. Mater. Interfaces* **2016**, *8*, 32031.
[95] Z. Zhao, J. Lai, D. T. Ho, Y. Lei, J. Yin, L. Chen, U. Schwingenschlögl, H. N. Alshareef, *ACS Energy Lett.* **2023**, *8*, 608.
[96] J. Chen, W. Zhou, Y. Quan, B. Liu, M. Yang, M. Chen, X. Han, X. Xu, P. Zhang, S. Shi, *Energy Storage Mater.* **2022**, *53*, 629.
[97] L. Zheng, H. Li, X. Wang, Z. Chen, C. Hu, K. Wang, G. Guo, S. Passerini, H. Zhang, *ACS Energy Lett.* **2023**, *8*, 2086.
[98] a) S. Liu, J. Vongsvivut, Y. Wang, R. Zhang, F. Yang, S. Zhang, K. Davey, J. Mao, Z. Guo, *Angew. Chem., Int. Ed.* **2023**, *62*, 202215600; b) L. Cao, D. Li, E. Hu, J. Xu, T. Deng, L. Ma, Y. Wang, X.-Q. Yang, C. Wang, *J. Am. Chem. Soc.* **2020**, *142*, 21404.
[99] D.-S. Liu, Y. Zhang, S. Liu, L. Wei, S. You, D. Chen, M. Ye, Y. Yang, X. Rui, Y. Qin, C. C. Li, *Adv. Funct. Mater.* **2022**, *32*, 2111714.

Huihua Li is currently an associate professor at the Harbin University of Science and Technology. She received her Ph.D. in physical chemistry from Karlsruhe Institute of Technology (Germany) in 2022. Afterward, she worked as a postdoctor in the Helmholtz Institute Ulm (Germany). Her current research interests are focused on electrolyte and novel electrode materials for sustainable rechargeable sodium batteries.

Zhen Chen is currently a professor at the Harbin University of Science and Technology. She received her B.S. degree at the Southeast University (SEU) in China in 2014, and Ph.D. degree at the Nanyang Technological University (NTU) in Singapore in 2018. From 2019 to 2022, she worked as a scientist at the Helmholtz Institute Ulm (HIU), Karlsruhe Institute of Technology (KIT) in Germany. Her research activities mainly focus on the development of key materials and relevant applications in the field of electrochemical energy storage with a special focus on developing high-performance solid-state secondary batteries.

Stefano Passerini is a professor at the Chemistry Department of Sapienza University of Rome. Formerly a professor at the Karlsruhe Institute of Technology, Helmholtz Institute Ulm (Germany) and the University of Muenster (Germany), he cofounded the MEET battery research center. His research focuses on the basic understanding and development of materials for high-energy batteries and supercapacitors, with the goal to create sustainable energy storage systems from environmentally friendly and available materials and processes. He is an internationally recognized pioneer in the field of ionic liquids and the development of alkali-ion batteries.

Huang Zhang is currently a professor at the Harbin University of Science and Technology, and formerly an associate professor at the Northwestern Polytechnical University (China). He has been a predoctoral research fellow in KU Leuven (Belgium). Afterward, he received his Ph.D. in 2018 from the Karlsruhe Institute of Technology (Germany) and then worked as a junior scientist in the Helmholtz Institute Ulm (Germany). His current research interests focus on the electrochemistry and materials chemistry in advanced and sustainable batteries.