Historical development and novel concepts on electrolytes for aqueous rechargeable batteries†

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In battery systems, aqueous electrolytes are superior in ionic conductivity, interfacial wettability, safety and environmentally benign compared to organic liquids, polymers, inorganic solid-state and ionic liquid electrolytes. However, their narrow electrochemical stability window, electrode dissolution/side reactions and temperature-variation instability result in a low energy density, undesirable cyclic lifespan and limited working temperature window in aqueous rechargeable batteries. Herein, the historical development of aqueous electrolytes in various types of batteries, ranging from monovalent-ion batteries, multivalent-ion batteries, metal–air batteries, metal–chalcogen batteries, and hybrid batteries to redox flow batteries is summarized through the representative pioneering works. Meanwhile, the strategies of electrolyte additive, pH-management, salt-concentrated electrolyte, gelling, solvent hybridizing, interface tuning and beyond concentrated electrolyte to mitigate the challenges associated with aqueous electrolytes are reviewed and discussed in detail. All these new electrolyte concepts mutually stabilize aqueous rechargeable batteries and improve their corresponding energy density in a broad temperature range, ushering in a promising aqueous energy storage era.

1. Introduction

Climate change has attracted global attention, and hence under the UN Paris Agreement, countries are committed to restricting global warming to less than 2 °C and are actively pursuing a 1.5 °C limitation. This has triggered a boom in research and practice towards carbon dioxide mitigation, ranging from carbon avoidance (photovoltaic power stations and hydrogen energy) and carbon embedding (methanol) to carbon removal (bioenergy crops and carbon capture technology). The popular strategy of using electric energy in automobiles, which are known as electric vehicles (EVs), can reduce the overall energy usage by enhancing energy efficiency, thus reducing carbon emissions, which can also be categorized into carbon avoidance. Transport is the second largest source of CO₂ emissions, with 24% of the total emissions, where the fuel efficiency of the mode of travel can significantly influence CO₂ emissions largely. Compared with current internal combustion engine vehicles, EVs are expected to reduce well-to-wheel emissions by...
70–85% by 2030 with virtually zero tailpipe emissions and excellent energy utilization efficiency, which requires the total use of EVs in the transport sector.\textsuperscript{5} The commercialization of EVs, involving full battery electric vehicles (BEVs), hybrid electric vehicles (HEVs) and hybrid plug-in electric vehicles (HPEVs), demands mature battery technology with the properties of high energy density, high power density and long lifespan, which currently, commercialized batteries especially lithium-ion batteries (LiBs) fail to satisfy.\textsuperscript{7,9,10}

In fact, the bottleneck in promoting the use of EVs promotion is the battery requirements, given that the current batteries exhibit undesirable energy densities, low power densities and safety issues, which are caused by the relatively low capacity of their positive electrode, sluggish electrode kinetics and/or electrode/electrolyte interface kinetics, and flammable organic solvent of electrolytes, respectively.\textsuperscript{11–15} Furthermore, although the cyclic lifespan of commercial LiBs (electrode) is acceptable, the degradation of their electrolyte can shorten the lifespan of a whole cell and even induce potential safety hazards.\textsuperscript{13,14} Concerning these issues, several new concepts ranging from lithium//air batteries, lithium//sulfur batteries and flow batteries (innovations on the cathodes)\textsuperscript{16–18} to solid-state batteries, quasi-solid-state batteries and aqueous batteries (innovations in the electrolyte) have been proposed and widely researched.\textsuperscript{19–21} Meanwhile, the capacity of the cathode is influenced by the interfacial kinetics and mass transportation between the electrolyte and cathode, where the working potential of the cathode will decrease due to interfacial polarization, thereby reducing the energy density of the whole cell.\textsuperscript{22,23} Therefore, electrolytes are of paramount importance for the development of batteries with high energy density and good safety.

An ideal electrolyte material should possess properties such as good electronic insulation, high ionic conductivity, wide electrochemical stability window (ESW), thermal stability and safety, facilitate interfacial kinetics, low chemical “cross-talk” between electrodes, be produced \textit{via} simple large-scale manufacturing process, inexpensive, environmentally friendly and non-toxic,\textsuperscript{24,25} however, currently no electrolyte can meet all these criteria. The conventional electrolytes can be classified into organic liquid electrolytes, polymer electrolytes, inorganic solid-state electrolytes, ionic liquid electrolytes and aqueous electrolytes, which are semi-quantitatively compared in Fig. 1. Among them, aqueous electrolytes are impressive in terms of their ionic conductivity, environmentally benign nature and interfacial wettability.\textsuperscript{26–33}

Exploring safe and cost-effective electrochemical energy storage systems is of great significance and importance.\textsuperscript{34,35} Based on aqueous electrolytes, aqueous rechargeable batteries (ARBs) have move to the forefront, which are destined to avoid the potential flammability and explosion of organic liquid electrolyte-based batteries and sophisticated (atmosphere controlled) manufacturing processes.\textsuperscript{36,37} Furthermore, due to the high permittivity and low viscosity of water, the ionic conductivity of aqueous electrolytes is considerably higher than that of organic liquid electrolytes, resulting in an excellent rate capability and power density in ARBs.\textsuperscript{29,36} Thus, based on the above-mentioned advantages of aqueous electrolytes, ultrafast charge–discharge energy storage systems can be established on a grid-scale with ARBs.\textsuperscript{29,38} However, there is a noticeable gap between conventional LiBs and ARBs in terms of energy density, which restricts the large-scale application and eliminates the low cost and good safety benefits of ARBs in the EV industry.\textsuperscript{39,40}

The relatively low energy density of ARBs is basically derived from the low working voltages caused by their narrow ESWs, which is related to the oxygen evolution in high-potential and
hydrogen evolution in low-potential aqueous electrolytes. To some extent, the narrow ESWs of aqueous electrolytes is the Achilles’ heel in improving the energy density of ARBs.\textsuperscript{36,41} In 2013, Wu et al. innovatively utilized a sandwich polymer membrane and LISICON to coat an Li metal anode. Due to the “cross-over” effect of the Li ion in the coated LISICON, this ARB delivered an output voltage of about 4.0 V, a big breakthrough in the theoretically ESW of water; however, it exhibited poor cyclic stability.\textsuperscript{42} Furthermore, the issue regarding the ESW can induce a short cyclic lifespan, thus increasing the cost to run energy storage stations based on ARBs.\textsuperscript{43} It is noteworthy that electrode dissolution in aqueous electrolytes can hinder the long-term charge–discharge cycling due to the strong polarity of water molecules. Theoretically, mass dissolution is a thermodynamically favorable process, as determined by the Gibbs free energy, regardless of the acid/alkaline environment of the electrolyte in real situations.\textsuperscript{44,45} Besides narrow ESWs and electrode dissolution, batteries can become unstable due to the side reactions of the electrodes with water and/or oxygen, especially in the case of aqueous rechargeable lithium-ion batteries (ARLiBs).\textsuperscript{41} Moreover, the phase transition of water with a variation in temperature can limit the application of ARBs at elevated or subzero temperatures, thereby confining the operation temperature windows of aqueous electrolytes.\textsuperscript{46} Hereon, the methods that can be employed to increase the energy density, expand the cyclic lifespan and extend the working temperature window of ARBs by tailoring aqueous electrolytes are summarized and discussed. Before that, the design concepts (principles) and historical development of aqueous electrolytes are briefly introduced and summarized in the following section.

2. Design concepts and historical development of aqueous electrolytes

2.1. Principles of battery electrolyte

The typical liquid electrolyte used in rechargeable batteries, fuel cells, and electrochemical capacitors is composed of a solvent, anion, and solvent-solvated cation. In the case of organic liquid electrolytes, the solid electrolyte interface (SEI) can function as a critical component to equip electrolytes with both electrochemical and thermal stability as well as excellent rate capability,\textsuperscript{47,48} which is absent in conventional aqueous electrolytes. Thus, a reasonable design is necessary for aqueous electrolytes, enabling good stability of the electrolyte/electrode interfaces. The design of an electrolyte is based not only on whether the reactants in both sides may be solid, liquid, or gaseous (processing consideration), but also the limiting electrochemical potentials \( \mu_A \) and \( \mu_C \) for the anode and cathode (their Fermi energies), respectively.\textsuperscript{49} The ESW of the electrolyte originates from the separation energy \( E_S \) of the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) of the electrolyte.\textsuperscript{50} Thus, to achieve thermodynamic stability in a battery, \( \mu_A \) and \( \mu_C \) should be located in the ESW of the electrolyte, as exhibited in the schematic illustration of the electron energies of the electrode and electrolyte in Fig. 2a. The open circuit potential \( (V_{OC}) \) of a battery cell can be defined as follows:\textsuperscript{51}

\[
e_{VOC} = \mu_A - \mu_C < E_a a
\]

where \( e \) is the magnitude of the electronic charge, while for organic liquid electrolytes, the passivating SEI film offers kinetic stability to a large \( V_{OC} \) with no extra-large.\textsuperscript{51} This is because an anode with a \( \mu_A \) above the LUMO can reduce the electrolyte unless a passivation layer generates a barrier to electron transfer from the anode to the electrolyte LUMO. Similarly, a cathode with a \( \mu_C \) below the HOMO will oxidize the electrolyte unless a passivation layer blocks electron transfer from the electrolyte HOMO to the cathode.\textsuperscript{51}

Experimentally, the ESW can be determined through standard potentiodynamic approaches such as linear sweep voltammetry (LSV) and cyclic voltammetry (CV), despite the various electrochemical environments of electrolytes during actual applications.\textsuperscript{52,53} The restricted reduction and oxidation potentials are assigned to a predefined value (reaching the decomposition current). The cutoff criteria may be arbitrary given that it lacks theoretical significance. In fact, the observed total current of the working electrode, \( i_T \), can be expressed as the sum of two parts, as shown in the following equation:\textsuperscript{53}

\[
i_T = i_{NF} + i_F
\]

where \( i_{NF} \) represents the nonfaradaic component (capacitive, interface double layer) and \( i_F \) represents the faradaic component (impurity reactions, redox process, and decomposition of the electrolyte at the interface).\textsuperscript{51} Ideally, \( i_{NF} \) should be close to zero if \( i_T \) indicates the ESW of the electrolyte exactly. Thus, practically, \( i_{NF} \) should be eliminated when predefining the current level for \( i_F \). Normally, \( i_{NF} \) and \( i_F \) can be distinguished by the slope of the LSV/CV curve. A lower slope in the LSV/CV curve is assigned to \( i_{NF} \), appearing earlier, whereas a higher slope is assigned to \( i_F \), appearing later.\textsuperscript{54,55} Also, non-porous electrodes such as Pt and glassy carbon can create the circumstance of \( i_{NF} \approx 0 \).\textsuperscript{53}

Conducting ions are the essential requirement of electrolytes, which affect how fast the energy stored in the electrodes can be delivered. In liquid electrolytes, the transport of ions is realized by the solvation and dissociation of ionic compounds and the migration of these solvated ions through the solvent.\textsuperscript{56} In terms of solvation and migration, ionic conductivity can be qualified as follows:\textsuperscript{57}

\[
\sigma = \sum_i n_i \mu_i Z_i e
\]

while for most liquid electrolytes, the conductivity results from the overall migration of both anions and cations. Also, for most batteries, only the portion of current carried by the cation is important, and thus the concept of transference number \( (I_{cation}) \) is introduced as follows:\textsuperscript{57}

\[
I_{cation} = \frac{R_{cation}}{\sum_i \mu_i}
\]
In diluted electrolyte, the transference number of cations is normally 0.2 to 0.4, meaning that anions are much more mobile than cations due to the solvation sheath around cations. A transference number of less than 1 can remarkably induce concentration polarization during battery operation through the resultant overwhelming anion movement and enrichment near the electrode surface, which requires a relatively “naked” cation with a high cation current.

Meanwhile, solvents with lower viscosity can enhance the mobility of ions and ameliorate the concentration polarization according to the Stokes–Einstein relation, as follows:

$$m_i = \frac{1}{6\pi\eta r_i}$$

where $r_i$ is the solvation radius. A lower $\eta$ leads to a higher $m_i$, while a lower solvation degree of cation (solvation radius) leads to a higher $m_i$. Besides, the dielectric constant, $\varepsilon$, of the solvents is also critical, which determines the charge carrier number ($n_i$). With a higher $\varepsilon$, ions have a higher probability of remaining free. Therefore, in terms of ionic conductivity, an ideal solvent should demonstrate a high $\varepsilon$ and low $\eta$, which is difficult to realize in organic solvent systems, while water can be an optimized option, thereby offering desirable ionic conductivity to high power density ARBs.

The ion conduction mechanisms between liquid and solid electrolytes are different. The potential energy profile of mobile ions in liquid electrolytes can be considered flat (Fig. 2b, right) due to the reasonably fast exchange between the solvating molecules and the solvent molecules, and the uniform surroundings. In contrast, the diffusion of mobile species in a solid-state crystalline network needs to pass through periodic bottleneck points, which define an energetic barrier that separates two local minima (typically crystallographic sites for ions) along the minimum energy pathway (Fig. 2b, left). Therefore, the ion conduction mechanism in liquid electrolytes is concentration diffusion, whereas in solid especially crystal solid electrolytes is ion hopping between the ground-state stable sites and/or intermediate metastable sites of the crystalline framework. In the crystalline case, vacancies of cations or interstitials are perceived as the mobile charged species, the migration mechanisms of which can be summarized as ion migration to a neighboring vacant site, direct interstitial mechanism between sites not fully occupied and concerted or correlated interstitially (knock-on) mechanism.

The ionic conductivity of a solid crystal electrolyte can be thermally activated, the process of which is described by a modified Arrhenius relationship, while the ion absolute mobility, $\mu$, can be linked to the ion diffusion coefficient, $D$, through the Nernst–Einstein relationship.

In the case of polymer and glass, which are two solid electrolytes exhibiting no long-range structural order, their mechanisms vary accordingly. In polymer electrolytes, the
relationship curve between $\sigma$ and $1/T$ is bent and is best fitted to VTF behavior (after Vogel, Tammann, and Fulcher). $T_o$ (equilibrium glass-transition temperature) is introduced for amendment, which is related to the (kinetic) measured glass-transition temperature. Glass is a promising electrolyte for use in solid-state batteries. Although the Arrhenius relationship and Nernst–Einstein relationship can still be applied to glass electrolytes, cation migration occurs via a mechanism that combines the concerted motion of cations with the large, quasi-permanent reorientation of anions. This effect, known as the ‘paddlewheel’ mechanism, is typically observed in high-temperature crystalline polymorphs. In contrast to the behavior of crystalline materials, the glass paddlewheel dynamics contribute to ion mobility at room temperature. The dynamics of ion motions in these materials are often described as being strongly coupled to the structural modes, whereas intermediate degrees of coupling are observed in organic ionic plastic crystals. Owing to the relatively weak interactions between molecules, reorientational processes occur with little hindrance. The orientations of molecules in ordered phases and rotor phases are illustrated in Fig. 2c. Recently, in one study, a unified framework was built for all liquid and solid (crystal, polymer, and glass) electrolytes based on the concepts of solvation shell for liquids and solvation cage for solids. An LiTFSI aqueous solution, $\beta$-Li$_3$PS$_4$ at 537 K, amorphous Li$_3$PS$_4$ glass at 298 K and LiTFSI in polyethylene oxide (PEO) at 363 K were utilized as examples in that work for liquid, crystal, glass and polymer, respectively (Fig. 2d), to study the Li-ion solvation structure. The ultimate goal was enabling the rational design of the solvation environment to propel the migration of the working ions in a unified framework.

Based on this design concept, numerous aqueous electrolytes have been developed and applied in various types of ARBs. In the following sections, the historic development of aqueous electrolytes is summarized in different types of ARBs, ranging from monovalent-ion batteries, multivalent-ion batteries, metal/air batteries, metal/chalcogen batteries, and hybrid batteries to redox flow batteries.

2.2. Monovalent-ion battery

Among the monovalent-ion batteries, LiBs are the most popular and practical, while sodium-ion batteries (SiBs), potassium-ion batteries (PIBs), even proton batteries (PbBs) and ammonium-ion batteries (AiBs) are starting to play an important role at this stage owing to the growing concern regarding lithium resources, manipulating the development of the corresponding aqueous electrolytes.

In 1994, the first ARLiB was introduced by Jeff Dahn and co-workers with VO$_2$/LiMn$_2$O$_4$ chemistry in 5 M LiNO$_3$ aqueous solution, delivering an energy density of 75 W h kg$^{-1}$, which was regarded as a breakthrough in energy storage systems. In 2009, Na$_2$SO$_4$ aqueous solutions were employed as electrolytes for realizing Na$^+$ reversible intercalation/deintercalation in an NaMnO$_2$ cathode, which were further developed in 2010, coupling an NaTi$_2$(PO$_4$)$_3$ anode and Na$_4$Mn$_2$O$_7$ cathode. Compared with lithium, sodium offers multiple advantages ranging from its wide abundance in the Earth’s crust and dramatically lower cost to even distribution worldwide, and hence has attracted a great deal of attention. Meanwhile, K$_2$SO$_4$ aqueous solution facilitated K$^+$ reversible intercalation/deintercalation in the K$_{0.27}$MnO$_2$ cathode in 2010. Subsequently, a Prussian blue analogue (PBA), nickel hexacyanoferrate was proposed to function as a cathode for PbIB with 1 M KNO$_3$ aqueous electrolyte. Its open-framework structure allowed the retention of 66% of the initial capacity even at a C rate of 41.7. The high power density, safety, and low-cost production method of this device make an attractive candidate for use in large-scale energy storage to support the electrical grid. Proton insertion/extraction involving electrochemical energy chemistries have been reported as hybrid devices, until the discovery of a pure proton rocking-chair capacitor with anthraquinone (AQ)/tetrachlorohydroquinone (TCHQ) redox couple and 0.5 M H$_2$SO$_4$ aqueous electrolyte. Recently, 62 wt% (9.5 m, molality, molar salt in kg solvent) H$_3$PO$_4$ was reported as an electrolyte for a high-rate aqueous proton battery, with Mn$_2$O$_3$ as the anode and CuFe-Turnbull’s blue analogue (H-TBA) as the cathode.

2.3. Multivalent-ion Battery

The energy density of multivalent-ion batteries (MViBs) is theoretically higher than that of the presently commercialized LiBs due to the higher capacity induced by the multivalent ion insertion in the cathode. Magnesium (Mg), aluminum (Al), calcium (Ca) and zinc (Zn) ion batteries dominate among the MViBs, while iron (Fe) and copper (Cu) ion batteries have also emerged recently. Similar with ARLiBs, aqueous electrolytes make MViBs safe and environmentally friendly, even perform bettering than ARLiBs because of their higher energy density, and hence water in MViBs can open doors to new opportunities. Among them, aqueous rechargeable zinc-ion batteries (ARZiBs) can be further selected as the crown jewel due to their features of high abundance, large-scale production, nontoxicity, low redox potential (−0.76 V vs. standard hydrogen electrode (SHE)) and high overpotential for hydrogen evolution.
reactions (contributing to the thermodynamic stability against aqueous electrolytes). Alkaline Zn//MnO2 batteries with KOH aqueous solution served as the primary battery since the 1960s, and efforts to make them rechargeable started in the 1990s, even expanding manganese-based cathodes to vanadium-based materials and PBA. In the last three years, remarkable progress has been achieved in the case of ARZiBs, especially for aqueous Zn–MnO2 batteries through the technical routines towards aqueous electrolytes such as hydrogel, salt-concentrated, pH-adjusting and decoupling electrolytes. Some representative works are exhibited with the employed electrolytes and compared in terms of energy density and lifespan (cyclic number) in Fig. 3, where the energy density of various aqueous Zn//MnO2 batteries is unified based on the mass of MnO2, and some of them are basically estimated. There is an obvious tendency to employ aqueous Zn//MnO2 batteries as high-energy storage devices, which are almost ready for further commercialization on a large scale, while their flexible and stretchable properties enabled by hydrogel electrolytes extend their applications from electric grids to daily-use, wearable electronic devices.

Besides Zn, Al is also an abundant and cheap element, which possesses a superior volumetric capacity to that of Mg and Ca. As early as around 1980, an NaCl aqueous solution was used as the electrolyte for Al-alloy//air batteries. In 2012, Liu et al. demonstrated Al-ion insertion/extraction in anatase TiO2 electrode with an AlCl3 aqueous solution as the electrolyte; however, it is highly acidic in nature and enhances the dissolution of the active material and corrosion of auxiliary battery parts. To overcome this drawback, Al(NO3)3 and Al2(SO4)3 aqueous solutions have been developed as electrolytes for aqueous rechargeable aluminum-ion batteries (ARAIbS). However, the corresponding electrochemical activity was weakened in these electrolytes, especially for Al-ion insertion/extraction in anatase TiO2 electrodes. Therefore, mesoporous nanosized electrodes have been demonstrated to improve the electrode and interfacial kinetics, and thus enhance the discharge capacity. Mg is regarded another alternative to Li, but it suffers a lot from sluggish kinetics in organic liquid electrolytes. Therefore, water was introduced in a non-aqueous system to enhance the kinetics in electrolytes and cathodes, and thus the rate capability of the whole cell. Since 2013, numerous works focused on aqueous Mg chemistries have been reported in half-cells (mostly using Mg(NO3)2 aqueous solutions as electrolytes); however, it was only in 2017 that Chen et al. reported the fabrication of a full Mg-ion battery (MiB) based on 1 M MgSO4 aqueous solution with a polyimide/nickel hexacyanoferrate redox couple. In the same year, Wang et al. used a 4 m (molar salt in kg solvent) magnesium bis(trifluoromethane sulfonyl)imide (Mg(TFSI)2) super-concentrated electrolyte to expand the ESW to 2.0 V, enabling poly pyromellitic dianhydride//lithium vanadium phosphate battery chemistry with a working voltage of 1.9 V. Likewise, water was introduced in a Ca ion battery to improve the electrolyte and electrode/electrolyte kinetics, while a super-concentrated aqueous electrolyte (8.37 m Ca(NO3)2) was used with a CuHCF working electrode in a half-cell system, delivering a capacity of almost 70 mA h g\(^{-1}\). In 2017, the combination of 2.5 M Ca(NO3)2 aqueous electrolyte with an organic polyimide anode and CuHCF cathode as a full cell was reported, displaying 1000 cycles of charge–discharge under 400 mA g\(^{-1}\) current density with a cut-off voltage of 0.5–1.9 V. Among the metal elements used as cations (charge carriers) in MVIbS, Fe element is even more abundant than Zn, Mg and Ca, which has a content of ~46.500 ppm in the
Earth’s crust.84 Reversible Fe plating/stripping was realized in an FeSO₄ aqueous electrolyte with Fe-based PBAs, which exhibited an excellent cycling performance of 1000 cycles. The authors also showed that the Fe metal anode could pair with an LiFePO₄ cathode as a hybrid cell, displaying a discharge capacity of ~155 mA h g⁻¹.84 In summary, ARZiBS and ARAiBs are more suitable to be industrialized than the other types of ARBs at this stage in terms of reliable performance and cost. Particularly, ARZiBS are almost ready for application in portable electronic devices and large-scale energy storage stations, especially Zn//MnO₂ batteries, as shown in Fig. 3, but their energy density needs to be further improved for EV applications.

2.4. Metal//air battery

Since the 1960s and early 1970s, considerable work has been carried out on metal//air batteries (MABs) for a variety of applications.117 MABs are unique compared with other batteries owing to the fact that their electroactive material (oxygen) does not require storage. In this respect, this type of battery is similar to fuel cells and is essentially a fuel cell/battery hybrid, which principally simplifies the battery design and increases the energy density.117 Therefore, MABs have attracted much attention as a possible alternative due to their extremely high energy density compared to that of other batteries, as shown in Fig. 4a.118 The electrolytes utilized for MABs can be basically classified into aqueous electrolytes (not sensitive to moisture) and non-aqueous electrolytes (water-sensitive system with aprotic solvents). Li and Na are intrinsically suitable for non-aqueous electrolytes, while metals such as Al, Fe and Zn are appropriate for aqueous systems.118 For the first time, a water-stable Li metal anode with water-stable lithium-conducting glass ceramics (Li super ion conductor, LISICON) and a lithium-conducting polymer electrolyte was proposed as the anode for an Li//air battery (LAB) with LiCl aqueous electrolyte at the air electrode in 2008,119 possessing a similar cell configuration to that shown in Fig. 4b. Although the nonaqueous electrolyte-based LABs possessed a higher energy density/power density than that of the aqueous electrolyte-based LABs, the uncertain side reactions in the oxygen electrode and aprotic solvent-insoluble Li₂O₂, which usually occur in the former, can be avoided in the latter.120 In 2014, the application of a gel polymer/LISICON multilayer-coated Li metal anode was expanded to an Li/Br₂ battery with 1 M LiBr₂ as the electrolyte.121 Based on a similar design concept, in 2013, a mixed aqueous (NaOH)/aprotic electrolyte was realized through a separator of Na₃Zr₂Si₂PO₁₂ (NASICON) ceramics and applied in an Na//air battery (SAB), discharging a capacity of ~600 mA h g⁻¹ (energy density of ~1500 W h kg⁻¹) and outputting an areal powder density of 11 mW cm⁻².122 Unlike LABs and SABs, Zn//air batteries (ZABs) naturally suit aqueous electrolytes, which mostly operate in alkaline media, such as KOH and NaOH, due to the higher activity of both the zinc electrode and air electrode since the first invention in 1878.123 The structures of cells based on alkaline aqueous electrolytes are much simpler than that of aqueous LABs and SABs, as shown in Fig. 4c, because no protection layers are required for Zn metal anodes. For ZABs with open structures, water loss from the aqueous electrolyte is a crucial cause of performance degradation, whereas the alkalinity of these electrolytes leads to the problem of insoluble carbonate precipitation and promotes zinc-dendrite growth and hydrogen evolution, all limiting the performance of ZABs.124 Thus, to overcome these problems through electrolytes, a molten Li₀.₆₇Na₀.₆₃K₀.₅₀CO₃ eutectic electrolyte with added NaOH was prepared and employed in a ZAB, which was cycled for 110 cycles.
at 550 °C, having an average charging potential of ~1.43 V and discharge potential of ~1.04 V.\textsuperscript{125} The relevant cell configuration is shown in Fig. 4d, together with the CV curve upon Zn plating/stripping (~1.38 V vs. Ni/\( \text{Ni(OH)}_2 \)) for zinc deposition and ~0.7 V vs. Ni/\( \text{Ni(OH)}_2 \) for the oxidation of Zn to Zn\textsuperscript{2+}.\textsuperscript{125} Al and Fe are deemed as the first and second most abundant metallic elements in the Earth’s crust. The theoretical energy density of Al/air batteries (AABs, 8140 \( \text{W h kg}^{-1} \)) is much higher than that of ZABs (1350 \( \text{W h kg}^{-1} \)), while that of Fe/air batteries (IABs) is 1200 \( \text{W h kg}^{-1} \).\textsuperscript{126,127} Considering this, AABs should be more promising; however, they suffer significantly from self-corrosion of the anode and sluggish kinetics, which demand a rational electrolyte with good stability and electrode/electrolyte interface process. Initially, NaCl aqueous solution was utilized as the electrolyte for AABs, but the energy density was restricted in the neutral condition, and then an alkaline system was introduced for not only AABs (KOH) but also IABs (KOH + LiOH).\textsuperscript{117,128}

### 2.5. Metal/chalcogen battery

Besides MABs, metal/chalcogen batteries (MCBs) are promising alternatives because they can provide remarkable capacities, while using cheaper and more reliable electrodes of sulfur (S), selenium (Se) and tellurium (Te) than air electrodes.\textsuperscript{129,130} MCBs possess an exceptional energy density (for instance, 2600 \( \text{W h kg}^{-1} \) for Li/S batteries, LSBs) and may be readily integrated a photocatalyst in a hybrid LSB involving alkalic catholyte to store solar energy directly. At the Li anode side, an organic liquid electrolyte of 1 M LiClO\(_4\) in ethylene carbonate (EC)/dimethyl carbonate (DMC) was used, coupled with an Li\textsubscript{1.35}Ti\textsubscript{1.75}\textsubscript{Al\textsubscript{0.25}}P\textsubscript{2.7}Si\textsubscript{0.3}O\textsubscript{12} (LATP) glass ceramic separator.\textsuperscript{135} The structure of this solar energy directly stored LSB and the reaction mechanism is shown in Fig. 5a. For the Na metal anode-based LSB, 0.25 M Na\textsubscript{2}S\textsubscript{4} + 0.1 M NaOH aqueous electrolyte (catholyte) was matched with 1 M NaClO\(_4\) in EC: propylene carbonate (PC) + 5% fluoroethylene carbonate (FEC) organic electrolyte (anolyte) with the assistance of an NASICON membrane, as shown in Fig. 5b.\textsuperscript{136}

![Fig. 5](image-url)
This configuration for both LSBs and SSBs not only stabilized the Li/Na metal anodes in aqueous electrolytes, but also prevented dendrite formation and polysulfide shuttling and increased the utilization of the active materials.

Zn stands out among the aqueous systems, and recently aqueous Zn/chalcogen batteries have also become eye-catching, as reported by Zhi’s group. An aqueous Zn//S battery was initially realized using a “liquid film”-comprising ionic liquid encapsulated in a copolymer (working as the cathode, as shown in Fig. 3c) and 1 M Zn(TFSI)$_2$ aqueous electrolyte. This Zn/polymer electrolyte system delivered an extraordinary capacity of 1148 mAh g$^{-1}$ and an overwhelming energy density of 724.7 W h kg$^{-1}$ (calculated based on the cathode mass, under a current density of 0.3 A g$^{-1}$). The same aqueous solution (1 M Zn(TFSI)$_2$) was also used as the electrolyte of a Zn//Se battery, but its performance was undesirable. Thus, a 2 M Zn(TFSI)$_2$/polyethylene glycol (PEG)/water electrolyte was prepared, extending the ESW of the aqueous electrolyte and enhancing the performance of the Zn//Se battery. The overall reaction mechanism of this battery was also studied, as follows:

$$\text{Zn + Se} \leftrightarrow \text{ZnSe}$$  \hspace{1cm} (6)

which was same conversion reaction mechanism in both the organic electrolyte and aqueous electrolyte. Meanwhile, an aqueous Zn/Te battery was also reported by Zhi’s group, utilizing a 1 M ZnSO$_4$ polyamide (PAM) hydrogel as the electrolyte, which displayed an ultra-flat discharge plateau and high volumetric capacity (2619 mAh cm$^{-3}$ under 0.05 A g$^{-1}$ current density). This battery exhibited obvious flat discharge plateau and high volumetric capacity (2619 mAh cm$^{-3}$ under 0.05 A g$^{-1}$ current density). The overall reaction mechanism of this battery was also studied, as follows:

$$\text{ZnTe}_2 + \text{ZnTe} \leftrightarrow 2 \text{ZnTe}$$ \hspace{1cm} (7)

as demonstrated in Fig. 5d. This work presented a new direction to design conversion-type aqueous MCBs with high capacity, stable output potential, excellent rate capability and long cyclic performance.

### 2.6. Hybrid battery

Aqueous hybrid batteries (AHBs) are new members of the ARB family, attracting great interest from researchers, which can be classified into hybrid ion batteries (HiBs), dual ion batteries (DiBs) and capacitor batteries (CBs). Besides CBs integrating battery behaviour in one side and capacitor behaviour in the other side, the mechanism of HiBs and DiBs is similar to that of single-ion ARBs, while their electrolytes are composed of various electrochemically active ions, diffusing from the electrolyte to electrodes simultaneously (for DiBs) or individually (for HiBs). Compared with the ARBs of single ions, AHBs exhibit several significant benefits, which can be summarized as follows: (1) enhanced rate performance by combining the ions of sluggish diffusion with that exhibiting better kinetics; (2) superior coulombic efficiency (CE) by avoiding ion trapping; (3) high flexibility and adaptability (more options for electrode materials); (4) low cost due to the less occupancy of Li/other costly elements in the whole cell; and (5) wide applications (energy storage and lithium purification).

AHBs are the most popular among AHBs, which can be further divided into monovalent/multivalent ion batteries and monovalent/multivalent ion batteries. In 2013, Xia’s group initially reported two monovalent/multivalent systems (Na$_{0.22}$MnO$_2$//LiMn$_2$O$_4$ and TiP$_2$O$_7$/Na$_{0.4}$MnO$_2$) based on Li$_2$SO$_4$ + Na$_2$SO$_4$ mixed electrolytes, exhibiting a specific energy of 17 W h kg$^{-1}$ and 25 W h kg$^{-1}$ based on the total weight of the active electrode materials, respectively. In 2018, a low-cost aqueous Mg–Na battery was proposed as a monovalent/multivalent system, employing Mn$_3$O$_4$ as the cathode of MiB, NaN$_2$(PO$_4$)$_3$ as the anode of SiB and 2 M MgSO$_4$ + 1 M Na$_2$SO$_4$ aqueous solution as the electrolyte, which avoided the cathode problems of SiBs and anode problems of MiBs. A Pb//LiMn$_2$O$_4$ battery was reported in 0.5 M Li$_2$SO$_4$ aqueous solution as a monovalent/multivalent system, which realized the reversible dissolution/deposition of Pb ↔ PbSO$_4$ in a neutral environment. Furthermore, an Mg//LiFePO$_4$ battery was developed in a hybrid electrolyte comprised of a non-aqueous electrolyte (1 M PhMgBr and 0.1 M LiBr in tetrahydrofuran) against an Mg anode and aqueous electrolyte (0.5 M H$_2$SO$_4$) against an LiFePO$_4$ cathode, while LISICON was utilized as the separator to stabilize both the non-aqueous and aqueous electrolytes.

In the case of monovalent/multivalent systems, Zn metal anode-based HiBs have been reported intensively, especially in mild aqueous electrolytes, which can overcome poor cyclic performances and the formation of Zn dendrites in alkaline conditions, as shown by the following equation:

$$\text{Zn} + 4\text{OH}^- \leftrightarrow \text{Zn(OH)}_4^{2-} + 2\text{e}^- \leftrightarrow \text{ZnO} + 2\text{OH}^- + \text{H}_2\text{O} + 2\text{e}^-$$  \hspace{1cm} (9)

In 2012, Chen et al. proposed Zn metal anode-based HiBs for the first time, which employed LiMn$_2$O$_4$ as the cathode and 3 M LiCl + 4 M ZnCl$_2$ solution (pH = 4) as electrolyte. Afterwards, aqueous Zn–LiMn$_2$O$_4$ batteries were investigated frequently, while the relevant reaction mechanism was determined as follows:

$$\text{Negative: } \text{Zn}^{2+} + 2\text{e}^- \leftrightarrow \text{Zn}$$ \hspace{1cm} (10)

$$\text{Positive: } \text{LiMn}_2\text{O}_4 \leftrightarrow \text{Li}_1.2\text{Mn}_2\text{O}_4 + x\text{Li}^+ + xe^-$$ \hspace{1cm} (11)

In 2018, Wang’s group made a breakthrough in aqueous Zn//LiMn$_2$O$_4$ batteries via the use of 1 m Zn(TFSI)$_2$ + 20 m LiTFSI highly concentrated electrolyte, which was cycled for 4000 cycles under a rate of 4C. In their work, a symmetrical Zn cell based on the highly concentrated electrolyte was cycled for 500 cycles (~170 h) under a current density of 0.2 mA cm$^{-2}$ without any dendrite and ZnO observed. The Zn-based monovalent/multivalent system was extended by Wu’s group from Zn/LiMn$_2$O$_4$ to the Zn/Na$_{0.38}$MnO$_2$ redox couple with 0.5 M Zn(OAc)$_2$ + 0.5 M
NaOAc electrolyte, which was charged/discharged for 1000 cycles under a rate of 4C in the voltage range of 1–2 V.148 Meanwhile, Wu's group made a noticeable contribution to rechargeable Zn-based HiBs in an alkaline environment, reporting the fabrication of Zn/Co3O4 and Zn/NiO batteries in 1 M KOH + 10 mM Zn(OAc)2 electrolyte with [Zn(OH)4]2− and OH− as the charge carriers.149,150 These works achieved a balance between high energy and high stability in alkaline battery systems.

The ions in HiBs participating in the electrode reaction are only cations, while both cations and anions are involved in DiBs, which need to be considered as active species. The typical cathodes of DiBs are graphite carbons, metal organic frameworks (MOFs), organic cathodes or electroactive polymers and MXenes, among which graphite carbon cathodes are the most suitable candidates for practical applications due to their unique layered structure, environmentally friendly nature, and low cost.151,152 An aqueous DiB using 1 M (NH4)2SO4 aqueous solution as the electrolyte was reported by Zhang et al. in 2019, in which the n-type polyimide anode reacted with NH4+, while the p-type radical polymer reacted with SO42− to obtain a large cell voltage of 1.9 V.154 Alternatively, Ji’s group made contributions to aqueous DiBs by using concentrated ZnCl2 aqueous solutions (30 m) with the ZnCl2− insertion molecular solid of ferrocene as the anode and Zn2+−insertion PBA as the cathode. This electrolyte not only minimized the dissolution of the ferrocene anode, but also widened the voltage of the full cell by 0.35 V compared with dilute ZnCl2 electrolyte.155 Both cations and anions contribute to the capacity in CBs, which is similar to that in DiBs, while the cations are involved in the redox-active oxide cathode and anions are absorbed/desorbed by an inert activated carbon (AC) anode in CBs. Therefore CBs is one type of relatively new device that is intermediate in energy between batteries and supercapacitors, whilst principally offering supercapacitor-like power and cyclability values.154 The high ionic conductivity of aqueous electrolytes can induce a high electrical double layer (EDL) capacitance in the active carbon anode/electrolyte interfaces, and hence can be a good option for CBs.29 An Li2SO4 aqueous solution was composed with an LiMnO2 cathode and AC anode as a Li+ ion capacitor by Wang and Xia in 2005,155 and before that, an Ni(OH)2 cathode was demonstrated as a good cathode for aqueous systems with an AC anode in alkaline aqueous electrolyte (KOH).156 Brousse et al. prepared a Na+ ion capacitor based on an Na2SO4 aqueous solution with AC anode, while MnO2 was utilized as a cathode for Na ion intercalation/deintercalation in the bulk according to the following equation:157

$$\text{MnO}_2 + 2\text{Na}^+ + 2\text{e}^- = \text{MnOO}_2\text{Na}$$  \hspace{1cm} (12)

while the surface redox could be enhanced once the cathode was nanosized as follows:

$$\text{(MnO}_2\text{)}_{\text{surface}} + \text{Na}^+ + \text{e}^- = \text{(MnOO}_2\text{Na)}_{\text{surface}}$$  \hspace{1cm} (13)

Recently, a Zn-ion capacitor was innovatively proposed by Kang et al., in which AC, Zn metal and ZnSO4 aqueous solution served as the cathode, anode and electrolyte, respectively. A metric of 121 mA h g−1 capacity (84 W h kg−1 energy density), 14.9 kW kg−1 power output and excellent cycling stability (over 10 000 cycles with 91% capacity retention) was exhibited.158 Numerous works towards Zn ion capacitors have been reported since then, indicating another feasible route to perfect electrochemical energy storage systems.

### 2.7. Redox flow battery

Redox flow batteries (RFBs) are novel electrochemical energy storage devices, storing electrical energy in two redox-active matters with distinct redox potentials. The redox species are usually dissolved or suspended in the electrolyte tanks (negaolyte and posolyte, as shown in in Fig. 6a). Electrochemical charge-transfer reactions occur on the electrode stack, consisting of a pair of porous electrodes separated by an ion-conducting membrane. The capacity of the RFB depends on the available charges stored in the electrolyte tank, whilst the current output of the RFB is determined by the rate of the electrochemical reaction on the electrode stack. This unique configuration enables design flexibility in decoupling energy and power, which is critical for large-scale energy storage and energy distribution.159 Aqueous redox flow batteries (ARFBs) are one of the most important candidates for large-scale energy storage, which can be applied over a wide power range with long lifetimes over a flexible discharge duration. Moreover, the natural scalability induced by their unique design of decoupled power and energy is considered the most prominent advantage. Since the first ARFB was invented by NASA in the 1970s with Fe(III)/Fe(II) and Cr(III)/Cr(II) as the active species and FeCl2- and CrCl3-containing HCl solution as the electrolyte, a vast number of ARFBs have been invented, which are classified as vanadium (V)-, Zn-, Fe-, polysulfide (PS)-based (inorganic) and organic-based ARFBs.160 In 1985, a V(III)/V(II) redox couple was introduced as the first V-based ARFB with VCl3-dissolved HCl/H2SO4 solution as the electrolyte, but there was considerable room for ameliorating the reversibility of the redox reactions.161 Furthermore, V-based ARFBs face the challenges of low thermal stability, crossover of V-species, and limited kinetics, which are basically correlated with the electrolyte issues, where porous nanofiltration-enhanced Nafion membranes (perfluorinated cation exchange membranes), as shown in Fig. 6b, can be the effective solutions.162,163 Besides V-based ARFBs, Zn-based ARFBs are widely reported due to the high adaptability of Zn metal anodes towards aqueous systems, and Zn//Br2 systems were the first to be reported among Zn-based species, in which KCl/NH4Cl-containing ZnBr2 concentrated solutions served as the electrolytes.164 However, Br2 is considered a hazardous substrate and the corresponding redox potential exceeds the ESW of water. Hence, Li et al. introduced Zn/I2 species with a battery structure scheme, as shown in Fig. 6c, consisting of a Nafion membrane and ZnI2 solution as the electrolyte. The redox mechanism was revealed as follows:165

\[ \text{Anode: Zn} \leftrightarrow \text{Zn}^{2+} + 2\text{e}^- \]

\[ E^0 = -0.7626 \text{ V vs. SHE} \]  \hspace{1cm} (14)
Cathode: \[ I_2(s) + I^-/C_0 \rightarrow I_3^-/C_0 + 2e^-/C_0 \]
\[ E^0 = 0.5360 \text{ V vs. SHE} \]  
Overall: \[ \text{Zn} + I_3^-/C_0 \rightarrow \text{Zn}^{2+} + 3I^-/C_0 \]
\[ E = 1.2986 \text{ V} \]  
with the relevant CV curve shown in Fig. 6d. In this case, ZnI$_2$ electrolytes with various concentrations were investigated, and the concentration of 3.5 M was selected for further cyclic performance tests due to the optimum CE, energy efficiency (EE) and voltage efficiency (VE) dependent on that condition, whereas ethanol was further added for expanding the stable electrolyte temperature window from $-20 \text{°C}$ to $50 \text{°C}$.

Similar to Zn-based ARFBs, Fe-based ARFBs have been widely studied and applied. As mentioned above, the initially studied ARFB was an Fe-based battery with Fe$^{3+}$/Fe$^{2+}$ and Cr$^{3+}$/Cr$^{2+}$ as the active species and HCl solution as the electrolyte, which was
limited by the sluggish reaction kinetics of \( \text{Cr}^{3+}/\text{Cr}^{2+} \), parasitic hydrogen evolution reaction (HER), and the crossover of active materials. Thus, management of the electrolyte pH was chosen as an effective strategy to mitigate these challenges,\(^\text{160}\) which will be discussed in detail in the next section. The first PS-based ARFB was invented by Regenesys Ltd in 1991 with NaBr on the positive side and \( \text{Na}_2\text{S}_4 \) on the negative side as the electrolyte,\(^\text{166}\) extending the utilization of PS from MCBs to ARFBs. Analogous to Zn-based ARFBs, the \( \text{Br}^-/\text{Br}_3^- \) chemistry was replaced by \( \Gamma^-/\text{I}_3^- \) in the PS system, demonstrating higher solubility, faster kinetics and a lower vapour pressure.\(^\text{167}\) This cell was comprised of KI and \( \text{K}_2\text{S}_2 + \text{KOH} \) aqueous solution and Nafion 115/117 membranes with the cell structure shown in Fig. 6e and CV curves of the redox species shown in Fig. 6f. Compared with inorganic-based ARFBs, organic-based ARFBs demonstrate large Earth abundance and high tunability through functionalization. In 2009, Xu et al. innovatively reported the concept of organic-based ARFBs by adopting 1,2-dihydrobenzoquinone-3,5-disulfonic acid (BDQS) or 1,4-dihydrobenzoquinone-2-sulfonic acid (BQS) as the cathode and conventional \( \text{PbSO}_4 \) in iron-containing aqueous \( \text{H}_2\text{SO}_4 \) solution as the anolyte, which delivered an average CE of 99% and EE of 70% over 100 cycles. The obtained high performance indicated that soluble quinones are promising positive materials for ARFBs.\(^\text{168}\) Recently, reversible ketone hydrogenation and dehydrogenation were realized in an organic-based ARFB using a design based on the molecular structure of 9-fluorenone (FL) as an example. An ARFB consisting of a ferro/ferricyanide catholyte and 1.36 M 4-carboxyl-7-sulfonate fluorenol (4C7SFL)/1 equiv. NaOH anolyte (equivalent to \( \text{H}_2\text{SO}_4 \)) added to 3 M \( \text{Zn(CF}_3\text{SO}_3)\) + 0.1 M \( \text{Mn(CF}_3\text{SO}_3) \) electrolyte, gelled electrolyte, solvent-hybrid electrolyte, electrolyte additive, salt-concentrated electrolyte, which equipped the HiB of \( \text{Zn}/\text{Na}_2\text{Mn-Fe(CN)} \) with a 2.0 V operation voltage and capacity retention of 75% over 2000 cycles. In this study, the surfactant additive could effectively suppress the oxygen evolution reaction (OER), and thus extended the ESW to 2.5 V, which was attributed to the SDS adsorption layer and theoretically confirmed by density functional theory (DFT) calculation, as shown in Fig. 9a-f.\(^\text{172}\)

3.1. Electrolyte additive

For conventional LiBs, the use of electrolyte additives is one of the most economic ways to improve their performance. Usually, the amount of additive in the electrolyte is no more than 5% either by weight or by volume, but it significantly improves the reversibility and cyclic life of LiBs.\(^\text{171}\) The strategy of electrolyte additives is also appropriate for ARBs, which was intensively reported in ARZiBs in the last five years. The additives added to aqueous electrolytes can be classified as ion, metal, organic and inorganic, offering the function of enhancing ion transportation, manipulating electrode interfaces, and tuning electrode surfaces/interfaces.\(^\text{172}\)

3.1.1. Suppressing OER on electrode surface. In a typical study on widening the ESWs of aqueous electrolytes, sodium dodecyl sulfate (SDS) was added to 1 M \( \text{Na}_2\text{SO}_4 + 1 \text{ M ZnSO}_4 \) aqueous electrolyte, which equipped the HiB of \( \text{Zn}/\text{Na}_2\text{Mn-Fe(CN)} \) with a 2.0 V operation voltage and capacity retention of 75% over 2000 cycles. In this study, the surfactant additive could effectively suppress the oxygen evolution reaction (OER), and thus extended the ESW to 2.5 V, which was attributed to the SDS adsorption layer and theoretically confirmed by density functional theory (DFT) calculation, as shown in Fig. 9a-f.\(^\text{173}\)

3.1.2. Inhibiting corrosion and dendrite formation in Zn metal anode. The above-introduced two additives expanded the ESWs by suppressing the OER, while additives such as \( \text{PbSO}_4 \), diethyl ether (Et\(_2\)O) and sodium dodecyl benzene sulfonate (SDBS) were used for inhibiting corrosion and suppressing the formation of dendrites in the Zn metal anode, thus enhancing the cyclability. \( \text{PbSO}_4 \) was added to 1 M \( \text{Li}_2\text{SO}_4 + 2 \text{ M ZnSO}_4 \) electrolyte gelled by 5% fumed silica until saturation, which provided a 20% lower corrosion current density on the Zn anode. The Zn metal anode in the tested \( \text{Zn}/\text{LiMn}_2\text{O}_4 \) HiB with \( \text{PbSO}_4 \)-containing electrolyte was determined to possess a dendrite-free morphology through scanning electron microscopy (SEM).\(^\text{174}\) In the \( \text{Zn}/\text{MnO}_2 \) system, 2 vol% Et\(_2\)O was added to 3 M \( \text{Zn(CF}_3\text{SO}_3)_2 + 0.1 \text{ M Mn(CF}_3\text{SO}_3)_2 \) electrolyte,
which was believed to be absorbed near the tip of the metal anode substrate surface, inducing an electrostatic shield and suppressing dendrite formation by maintaining a smooth deposition layer, as shown in Fig. 9g. SDBS was reported to improve the electrochemical behaviors of a Zn//LiFePO$_4$ HiB. With the assistance of this additive, Zn ions were deposited smoothly on the surface of the Zn metal instead of participating in the vertical growth of flake-shaped Zn dendrites. Simultaneously, the Li-ion diffusion coefficient was increased from $1.78 \times 10^{-11}$ to $8.22 \times 10^{-11}$ cm$^2$ s$^{-1}$ by ameliorating the wettability of the LiFePO$_4$ cathode, contributing to the high power density of the whole cell.  

### 3.1.3. Interfacial engineering

In LiBs, additives are used intensively for engineering interfaces, especially engineering SEIs, which are also employed to tailor the interfaces of ARBs. Recently, Wang’s and Xu’s group reported the use of trimethyl-ethyl ammonium trifluoromethanesulfonate (Me$_3$EtNOTF) as an additive in the fluorinated interface between a Zn metal anode and aqueous zinc trifluoromethanesulfonate (Zn(OTf)$_2$) electrolyte, which enabled the stable cycling of both a Zn//VOPO$_4$ full cell (136 W h kg$^{-1}$ and retained 88.7% of its capacity for >6000 cycles) and Zn//O$_2$ cell (325 W h kg$^{-1}$ for >300 cycles). The ZnF$_2$-rich composition in that interface was caused by the additive, while ZnCO$_3$, ZnSO$_3$, and poly-species.

---

**Fig. 7** Historical development of aqueous electrolytes with representative innovative works for various ARBs.
were also discovered there (Fig. 9h). DFT calculation suggested that the downstream reactions resulting from alkylammonium decomposition were responsible for the formation of ZnCO$_3$. In another work, ZnF$_2$ was added to 2 M ZnSO$_4$ electrolyte directly for the formation of a stable F-rich interfacial layer. The F-rich interfacial layer could not only regulate the growth orientation of zinc crystals, but also serve as an inert protection layer against side reactions such as the HER. Under the protection of that interfacial layer, Zn stripping/plating was stably repeated for 600 h, and an anode-free Zn//LiMn$_2$O$_4$ HiB was realized. Besides the interfaces between the Zn metal anode and aqueous electrolytes, the additive can also function on the cathode. In 2016, Wang’s group constructed a cathode electrolyte interphase (CEI) between an LiCoO$_2$ cathode and LiTFSI aqueous electrolyte through the electrochemical oxidation of tris(trimethylsilyl) borate. The LiCoO$_2$ cathode was stabilized at a high cut-off voltage corresponding to 0.7 $e^-$ electron charge transfer, which delivered a working voltage of 2.5 V and 120 W h kg$^{-1}$ energy density.

**3.1.4. Solvation sheath tailoring.** To widen the working temperature windows of ARBs, some efforts focused on tailoring their solvation sheath, which adjusted the correlated ARBs to the frozen environments. Dimethyl sulfoxide (DMSO), a highly polar aprotic solvent, can form strong H-bonds with water molecules and significantly change the original H-bond structure of water molecules. According to previous studies, the HER of water molecules is a competitive process with the H-bond formation process in solution, and hence DMSO is
an effective additive to suppress the HER. Thus, DMSO was added to an aqueous solution of 2 M NaClO₄ with a molar fraction of 0.3 (2M-0.3 electrolyte). The 2M-0.3 electrolyte exhibited a sufficient ionic conductivity of 0.11 mS cm⁻¹ at
−50 °C. The Raman and Fourier transform infrared (FTIR) spectra proved that hydrogen bonds were stably formed between DMSO and water molecules, facilitating the operation of the electrolyte at ultra-low temperatures, while molecular dynamics (MD) modelling, as shown in Fig. 9i, demonstrated consistent results.46 In ARFB systems, additives are also employed to widen their working temperature windows. For example, 10 vol% ethanol served as an additive in a near-neutr al 5 M ZnI₂ electrolyte of Zn/I₂ ARFB, enabling a stable battery performance in the temperature range of −20 to 50 °C. Nuclear magnetic resonance (NMR) study and DFT-based simulation together with flow test data illustrated that the addition of ethanol induced ligand formation between the oxygen on the hydroxyl group and the zinc ions, which not only extended the stable electrolyte temperature window but ameliorated the interface of the zinc metal anode.165 In the PB system, anions such as BF₄⁻ and SO₄²⁻ were discovered to enhance the adaptability of relevant aqueous electrolytes towards frozen conditions. In one work on a PB, FTIR, Raman and NMR analyses synergistically demonstrated that the introduction of BF₄⁻ anions efficiently broke the hydrogen-bond networks of the original water molecules, resulting in an ultralow freezing point. Therefore, the allaxazine/MnO₂ redox couple could run regularly even at −90 °C and displayed a high specific discharge capacity of 85 mA h g⁻¹.162 Similarly, the hydrogen bonds between water molecules in the electrolyte could be remarkably damaged by modulating the interaction between SO₄²⁻ and water molecules, lowering the freezing point of the electrolyte. Consequently, the p-chloranil-reduced graphene oxide redox couple of the proton insertion mechanism delivered an extraordinary electrochemical performance even at −70 °C.183 Basic ally, the electrolyte additive strategy can be a feasible route to improve the stability and widen working temperature windows of ARBs. The performance of representative works is summarized in Table S1 (ESI†). However, some additives probably fail to become a universal way to achieve better main aqueous electrolytes. Furthermore, electrolyte additiv es only function as minor modification to some cases rather than a fundamental transformation, while solvents and salts have a greater effect on aqueous electrolytes.

3.2. pH management and two-pH decoupling electrolyte

In aqueous electrolytes, the pH value can have a considerable impact on the ESW by thermodynamically affecting the HER and OER. Furthermore, the pH and H₂O in aqueous electrolytes with or without O₂ can influence the stability and working potential of the electrodes in ARLiBs, as follows:41

\[
\text{Li(incorporated) + } \frac{1}{4} \text{O}_2 + \frac{1}{2} \text{H}_2\text{O} \rightarrow \text{Li}^+ + \text{OH}^- \quad (17)
\]

Based on the chemical potential of intercalated Li in the electrode (μLi(x)) and Li in Li metal (μLi), the working potential of the electrode (V(x)) can be derived as follows:184

\[
V(x) = 4.268 - 0.059 \text{pH} (V) \quad (18)
\]

where x for both μLi(x) and V(x) is the amount of intercalated Li in the lithium-ion intercalated compounds. According to eqn (18), V(x) in equilibrium condition is determined to be 3.85 V at pH 7 and 3.50 V vs. Li/Li⁺ at pH 13, indicating that the reduction state of all usual anode materials in ARLiBs would theoretically be chemically oxidized by O₂ and H₂O rather than undergoing the electrochemical redox process. However, after eliminating O₂ in aqueous electrolytes, the reaction becomes:185

\[
\text{Li(incorporated) + H}_2\text{O} \leftrightarrow \text{Li}^+ + \text{OH}^- + \frac{1}{2} \text{H}_2 \quad (19)
\]

and the correlated V(x) can be further determined as:41

\[
V(x) = 3.039 - 0.059 \text{pH(V)} \quad (20)
\]

revealing that H₂O can also chemically oxidize some reduction-state anodes in ARLiBs.

3.2.1. pH management for higher stability. Theoretically, the pH value of aqueous electrolytes can serve as a benchmark to determine whether the electrodes are stable against the corresponding aqueous electrolytes. Practically, pH adjusting can be another route to manipulate the stability of ARBs.181 Base on this idea, Cui’s group used 1 M KH₂PO₄ (pH = 1) solution as an electrolyte for a Pb with a copper hexacyanoferrate cathode and AC/polypyrrole hybrid anode, which had zero-capacity loss after 1000 deep-discharge cycles.38 Xie et al. adjusted the pH value of 5 M LiNO₃ aqueous electrolyte by controlling the concentration of LiOH, and found that when the pH was −8.5, the ARLiB with the CuV₂O₅//LiMn₂O₄ redox couple demonstrated the optimum cyclic performance.186 pH management of aqueous electrolytes is also a popular strategy to stabilize ARFBs. For example, Xie et al. utilized a 1.5 M HAc/NaAc buffer electrolyte to maintain the pH value of negative electrolyte in a Zn/Fe-based ARFB in the range of 2.0–6.0. The chemical reaction of Zn species with proton species was very insignificant, while the electro-reduction of protons on the negative electrode was significantly suppressed in this pH range.187 In a PS-based ARFB system, PS could be stabilized in alkaline electrolyte by avoiding the formation of H₂S in neutral and acidic conditions. The equilibrium potential of polysulfide was pH-dependent for pH < 11.5, while it remained at −0.51 V vs. SHE when pH > 11.5. The reaction of PS in water was as follows:188

\[
\text{S}_2^{2-} + 2\text{H}_2\text{O} + 2e^- \leftrightarrow 2\text{HS}^- + 2\text{OH}^- \quad (21)
\]

In a Zn/I₂ ARFB, fast overcharge self-protection ability was demonstrated with a smart pH-responsive electrolyte. Once overcharged, the electrolyte pH increased, which was induced by hydrogen evolution, and consequently the irreversible formation of insulating ZnO at the anode side and soluble Zn(OI₂)₂ at the cathode side, which could rapidly switch off the Zn/I₂ ARFB with capacity degrading to 6% of the initial capacity, thereby avoiding continuous battery damage. Noticeably, the stimulus-responsive ARFB could be switched on with
nearly 100% capacity recovery by re-adjusting the electrolyte pH, delivering excellent stability.\textsuperscript{189}

### 3.2.2. pH management for higher energy density

Besides stability, pH management even can improve the energy density of ARBs, especially for the Zn/MnO\textsubscript{2} system, in which the cathode mechanism can be classified as proton-participating conversion in mild/strong alkaline environment,\textsuperscript{190,191} reversible Zn ion insertion/extraction in neutral/mild acidic aqueous electrolyte,\textsuperscript{94,192} proton and Zn ion co-insertion in mild acid condition,\textsuperscript{193} and cathode dissolution/deposition mechanism under strong acid condition.\textsuperscript{95,194} Various cathode mechanisms generate different working potentials in the cathode, among which the that of the dissolution/deposition mechanism is the highest. Therefore, the pH value of 1 M ZnSO\textsubscript{4} + 1 M MnSO\textsubscript{4} aqueous electrolyte was adjusted using H\textsubscript{2}SO\textsubscript{4} to create a strong acid environment, while 0.1 M was chosen as the optimized concentration of H\textsubscript{2}SO\textsubscript{4} for balancing between a high working voltage and wide ESW (desirable cyclic stability). The discharge profiles of the pH-adjusted electrolyte-based Zn–MnO\textsubscript{2} battery exhibited three discharge regions including D1 (2.0–1.7 V), D2 (1.7–1.4 V), and D3 (1.4–0.8 V), which represented MnO\textsubscript{2} dissolution, proton insertion, and Zn ion insertion, respectively (Fig. 10a). The average out-put voltage of that cell was 1.95 V, together with \(\sim 570 \text{ mA h g}^{-1}\) capacity (active matter of both cathode and anode), exhibiting \(\sim 409 \text{ W h kg}^{-1}\) energy density.\textsuperscript{95} Based on the dissolution/deposition mechanism of MnO\textsubscript{2}, a membrane-free Zn/MnO\textsubscript{2} ARFB was proposed for large-scale energy storage with the corresponding schematic illustration and digital image, and schematic cross-section of the cell shown in Fig. 10b and c, respectively.\textsuperscript{101}

#### 3.2.3. Two-pH decoupling electrolyte

Actually, the pH of aqueous electrolytes not only affect the working mechanism of the MnO\textsubscript{2} cathode but also the Zn metal anode. The redox potential of Zn stripping/plating is \(-0.76 \text{ V vs. SHE}\), while for Zn/Zn(OH)\textsubscript{2} conversion in an alkaline environment can be extended to \(-1.199 \text{ V vs. SHE}\).\textsuperscript{98} Thus, decoupling the working conditions of the MnO\textsubscript{2} cathode and Zn anode to enable both acidic MnO\textsubscript{2} and alkaline Zn redox reactions in a single cell can break the 2.0 V barrier of the aqueous Zn/MnO\textsubscript{2} battery. One design (Fig. 10d) used both an alkaline (6 M KOH + 0.2 M ZnO + 5 mM vanillin) and an acidic (3 M H\textsubscript{2}SO\textsubscript{4} + 0.1 M MnSO\textsubscript{4}) electrolyte in two chambers separated by a neutral (0.1 M K\textsubscript{2}SO\textsubscript{4}) electrolyte to avoid their neutralization. The neutral electrolyte chamber was encapsulated by two membranes (cation-exchange or bipolar membrane) with ion selectivity on each side. Basing on this design, the decoupled Zn/MnO\textsubscript{2} battery exhibited an exceptionally high open-circuit voltage of 2.83 V and a specific energy density of 1621.7 W h kg\textsuperscript{-1} (based on the active mass of MnO\textsubscript{2}).\textsuperscript{97} The three-chamber structure was sophisticated to some extent, and hence one study attempted to construct this type of decoupled Zn/MnO\textsubscript{2} battery into a ARFB with one anolyte of 2.4 M KOH + 0.1 M Zn(CH\textsubscript{3}COO)\textsubscript{2} and one catholyte of 0.5 M H\textsubscript{2}SO\textsubscript{4} + 1.0 M MnSO\textsubscript{4}, separated by a bipolar membrane (Fig. 9e).\textsuperscript{96} Recently, a poly-acrylate (PA)-based alkaline hydrogel and PAM-cellulose-based acid hydrogel were prepared and employed as a two-pH decoupling electrolyte. The commonly used cellophane worked as a separator, effectively solving the problem of electrolyte neutralization caused by diaphragm ruptures. The flexible Zn/MnO\textsubscript{2} battery displayed a high working voltage of 2.7 V, high area capacity of 2.63 mA h cm\textsuperscript{-2}, and acceptable cyclic stability of 86.7% capacity retention after 400 cycles.\textsuperscript{195}

The alkaline/acid decoupling electrolytes were designed for an aqueous Zn/MnO\textsubscript{2} battery, whereas alkaline/mild ones were proposed by Wu’s group for Zn–Li HiBs. In that system, 5 M LiNO\textsubscript{3} and 5 M LiOH + 1 M Zn(OAc)\textsubscript{2} aqueous solutions were selected as the cathodic and anodic electrolytes, respectively, coupling the waste Nafion NR117 membrane treated with 3 wt\% H\textsubscript{2}O\textsubscript{2} and 1 M H\textsubscript{2}SO\textsubscript{4} as the separator (Fig. 9f). Before that, the same membrane was employed in an aqueous Zn/MnO\textsubscript{2} battery and an aqueous Li-ion capacitor with alkaline/mild electrolytes, showing its feasibility and validity as a separator.\textsuperscript{196,197} While in the Zn–Li HiB, a Zn anode in alkaline solution and LiMn\textsubscript{2}O\textsubscript{4} cathode in mild solution together equipped the whole cell with a working voltage of above 2.3 V. This battery system delivered a steady energy density of 208 W h kg\textsuperscript{-1} (based on the total weight of active materials) at 1.69C with a high average output voltage of up to 2.31 V, and could be cycled for over 1000 cycles with an average CE of \textgreater98\%.\textsuperscript{198} In summary, the pH of aqueous electrolytes can influence the redox potential and even the reaction mechanism of electrodes, thereby influencing the stability and working voltages of the whole cell, which is an important move towards overcoming the disadvantages of ARBs. The performance of representative works is summarized in Table S2 (ESI†). However, managing the pH of aqueous electrolytes may fail to shift the electrode redox potential considerably according to eqn (18) and (20). In contrast, for two-pH decoupling electrolytes, their complicated cell structures probably restrict their application and popularization in ARBs, together with the unwanted HER and OER at the electrode/electrolyte interfaces under a high working voltage. Therefore, the strategies of pH management and two-pH decoupling electrolyte need more studies and further optimization to maturely enhance the stability and working voltage/energy density of ARBs.

#### 3.3. Salt-concentrated electrolyte

Liquid electrolytes are a combination of solvents and salts, while salt concentration is a critical parameter, impacting the ESWs, ionic conductivity, and electrode/electrolyte interfaces through solvation structures, viscosity, ionic mobility and overall electrolyte structure (morphology).\textsuperscript{36,199} Based on this, salt concentration manipulation is an easy and effective way to tailor the corresponding liquid electrolytes. Increasing the salt concentration in liquid electrolytes will result in enhanced interactions between cations and anions/solvents and a decrease in the content of free-state solvent molecules, which will demonstrate unusual physicochemical and electrochemical properties that are remarkably distinct from conventional dilute electrolytes.\textsuperscript{199}

#### 3.3.1. “Water-in-salt” electrolyte

In 2015, one significant breakthrough was made by Wang’s and Xu’s group, proposing...
the concept of “water-in-salt” electrolyte (WiSEs), which ushered salt-concentrated electrolytes and ARBs into a new era. The flourishing salt-concentrated electrolytes in ARBs can be categorized into WiSEs, hydrate-melt electrolytes (HMEs) and regular super-concentration electrolytes (RSCEs), which generate wide ESWs, and then high energy density. The definition of WiSEs is that salt outnumbers the solvent in a binary system in terms of both weight and volume, leading to an anion-containing Li-ion solvation sheath (Fig. 11a) and the formation of a dense interphase on the anode surface (mainly arising from anion
reduction, Fig. 11b). Combined with the substantially reduced electrochemical activity of water in a WISE of 21 m LiTFSI, an ESW of ~3.0 V was provided, which equipped a full ARLiB (Mo₆S₈//LiMn₂O₄) with a working voltage of 2.3 V and 1000 charge/discharge cycles. Since that, WiSEs have demonstrated all-round versatility in raising the energy density, enhancing the stability and widening the working temperature windows of ARBs. In terms of energy density enhancement, Wang’s and Xu’s groups applied WiSEs to an ARLiB with halogen conversion-intercalation chemistry in graphite, delivering a capacity of 243 mA h g⁻¹ (based on the total weight of the electrode) at an average potential of 4.2 V vs. Li/Li⁺. Pairing a graphite anode with an artificial SEI, a 4 V class ARLiB was created with an energy density of 460 W h kg⁻¹. Furthermore, Wang’s and Xu’s group employed the WiSE in ZAB chemistry with a porous carbon air cathode, demonstrating an energy density of 1000 W h kg⁻¹ (based on the mass of the cathode) in 200 cycles. Meanwhile, in the LAB system, WiSEs provide the necessary functionalities to support aprotic Li//O₂ operations via reversible Li₂O₂ formation and decomposition. The lack of organic solvent molecules was a highlight there, eliminating the known reaction pathways towards by-product formation in organic electrolyte systems.
solid–liquid two-phase, and LiMn2O4/LiCoO2 cathode, delivering a working voltage of 1.8/2.24 V (Fig. 11d). The capacity of the sulfur anode was tested as 1327 mAh g⁻¹, while the energy density of the full cell was determined to be 200 Wh kg⁻¹ (total electrode mass) for >1000 cycles at ~100% CE.²⁰¹

The stability endowed by WiSEs is also significant among ARBs, not only suppressing the HER/OER of water but also dissolution of the electrodes in aqueous electrolytes. In the above-described LSB system, excellent cyclic stability was induced by the solid–liquid two-phase reaction pathway, where the liquid polysulfide phase in the sulfide electrode was thermodynamically phase-separated from the WiSE.²⁰¹ The phenomenon of negligible polysulfide dissolution in WiSEs can also be discovered in SiB chemistry. Yue et al. investigated concentration-controlled cathode dissolution through a susceptible Na3V2(PO4)3 cathode, whose time-, cycle-, and state-of-charge-dependent dissolubility were evaluated by multiple electrochemical and chemical methods. In that study, a novel mechanism of interface concentrated-confinement was proven with WiSEs, which enhanced the cyclic stability of the NaTi2(PO4)3//Na3V2(PO4)3 full cell. The high viscosity, low vanadium ion diffusion, low polarity of solvated water and scarce solute-water dissolving surfaces in WiSEs (9 m NaOTf + 22 m tetraethylammonium triflate, TEAOTf), remarkably decreased the thermodynamic-controlled solubility, the dissolving kinetics, and physical space local mass interfacial confinement (Fig. 11e).²⁰² It was discovered that the WiSEs could reduce the O2 solubility in water and the kinetics of the oxygen reduction reaction (ORR) by slowing down O2 diffusion, as shown by the Koutecky–Levich equation.²⁰² Hence, the WiSE-based cells could work with an open configuration, which exhibited superior ability to dissipate heat and pressure and eliminated the risk of explosion.²⁰² Besides stability, WiSEs can also expand the working temperature windows of ARBs. A WiSE of 22 m KCF3SO3 (KFSI) and 3,4,9,10-perylenetetracarboxylic diimide (PTCDI) anode. Beside the impressive performance of 80 W h kg⁻¹ and superior capacity retention of 85% at 20C after more than 10 000 charge–discharge cycles at room temperature (RT), the full PiB was assembled in a pouch cell, demonstrating a superior performance at a wide temperature range of ~20 °C to 60 °C.²⁰³ In the study reported by Reber et al., a key factor limiting the application of WiSEs at low temperatures was recognized due to their salt crystallization tendency even near RT. Thus, 10 m sodium (fluorosulfonyl)(trifluoromethylsulfonyl)imide (NaPTFSI) with asymmetric anions was introduced into 25 m NaFSI with symmetric anions. Subsequently, an SiB based on the asymmetric anion optimized WiSE in combination with an NaTi2(PO4)3 anode and Na+(VOPO4)3F cathode demonstrated excellent capacity retention and high energy density down to a temperature of ~10 °C.²⁰⁴ However, in WiSEs, expensive organic salts were intensively used, which increased the cost of the whole cell. Some studies attempted to use cost-effective salts as substitutions, and obtained some notable achievements, especially for that based on acetates and chlorates. Ji’s group applied potassium acetate (KOAc) to form a WiSE, which was capable of cycling relevant PiBs up to 11 000 cycles under a current density of 1 A g⁻¹ with an ESW of ~3.2 V.²⁰⁵ Through blending with LiOAc and Zn(OAc)2, this acetate-based WiSE could be used in ARLiBs and Zn/MnO2 systems with desirable performances and potentials on a large scale.²²,²⁰⁶ Meanwhile, Ji’s group reported the preparation of ZnCl₂-based WiSE (30 m ZnCl₂), enabling a dendrite-free Zn metal anode with high CE and a novel DiB with high reversibility.²¹³,²¹⁷

3.3.2. Hydrate-melt electrolyte. Among the salt-concentrated systems, another significant electrolyte reported was HMEs, which utilize a eutectic system thereof. LiTFSI and LiN(SO2CF3)2Cl (LiBETI) salts were firstly selected for HMEs because these anions are weakly Lewis basic and only interact with Li⁺ weakly, thereby promoting the solvation of Li⁺ by water molecules rather than the abundant formation of ion pairs. Furthermore, the anions exerted a ‘plasticizing’ effect, avoiding the crystallization of the salts and hydrates. Fig. 11f demonstrates the miscibility limits of the blended LiTFSI–LiBETI salts in water at RT, while the eutectic composition of Li[TFSI]0.7(BETI)0.3 was determined to exhibit the highest miscibility, forming a stable, transparent liquid with an extremely low water content (H2O : Li⁺ = 2.0 molar ratio), equaling a water molar concentration of 10.1 mol L⁻¹ (Fig. 10f). Because of this low water concentration, the water molecules could be isolated from each other by the bulky anions, thus suppressing the activity of water by decreasing the opportunity for the formation of clusters of free water molecules. This HME equipped LiT0.5S0.5O1.5//LiNi0.5Mn1.5O4 redox couples with an upper limitation working voltage of 3.1 V and energy density of >130 W h kg⁻¹, within 100 cycles.²⁰⁸ Besides, the concept of HME was applied to SiBs and PiBs, employing Na[PTFSI]0.65[TFSI]0.35(OTf)0.1(THF)0.15 and K[PTFSI]0.14[TFSI]0.86(OTf)0.08(THF)0.82H2O hydrate melts with ternary anions including TFSI⁻, OTF⁻ and especially asymmetric the N(SO2CF3)(SO2C2F5)⁺[PTFSI]⁻ anion, which significantly expanded the ESWs to 2.7 and 2.5 V, respectively. Na[PTFSI] and K[PTFSI] with asymmetric anions normally possess high solubility, which is attributed to their high vibrational mobility and flexibility offered by their asymmetric structure, realizing Na and K hydrate melts at super-high concentration.²⁰⁹ The HMEs were also applicable in LABs, coupling LiSICON glass ceramic-protected Li metal anode and Ketjen Black (KB) cathode, which showed a low charge potential of ~3.16 V, a high discharge capacity of 38 mAh cm⁻², and a stable cyclic ability of 50 cycles with a capacity limitation of 1000 mAh g⁻¹ under a current density of 500 mAh g⁻¹.²¹⁰ After substituting into ZnCl₂ 2.33 H₂O, the HME could work with a Zn metal anode and Pt/C cathode as a ZAB, delivering a reversible capacity of 1000 mAh g⁻¹ (based on catalyst) over 100 cycles.²¹¹ In the WiSE system, a similar concept to HME was proposed, namely “water-in-bisalt” electrolyte (WiBSE), which could dissolve another unhydrated salt with similar chemical properties and form binary salt systems in the molten state with higher cation/water ratios. In the typical WiBSE of 21 M LiTFSI + 7 m LiOTf, a more compact SEI than that in WiSE was created, allowing a 2.5 V TiO2/LiMnO2 full LiB with an average discharge voltage of 2.1 V and an energy density of 100 W h kg⁻¹ (total electrode mass).²⁷ Additionally, the acetate could replace the organic FSI⁻ anion-based salts in WiBSEs,
while the cation-size effect on ESWs in the acetate system was further investigated.\textsuperscript{212}

### 3.3.3. Regular super-concentration electrolyte

Normally, the cation/water ratio of WiseEs and HMEs reach above 2.0 for aqueous electrolytes with a high salt concentration but fail to approach the ratio or meet the definitions of WiseEs/HMEs, which can be categorized as RSCEs. Pan et al. investigated the thermodynamic and kinetic contributions to the ESW of an LiNiO\textsubscript{2}-based RSCE (LiNiO\textsubscript{2}:H\textsubscript{2}O = 1:2.5) through MD simulation and spectral analysis. The local structure of the intimate Li\textsuperscript{+}–water interaction was discovered at a super-concentration, inducing (Li\textsubscript{5}(H\textsubscript{2}O)\textsubscript{7})\textsubscript{n} polymer-like chains rather than the ubiquitous hydrogen bonding between water molecules, thereby extending the ESW to 2.55 V.\textsuperscript{211} Based on RSCEs, a universal strategy was proposed to ameliorate the specific energy, reversibility and safety of MViBs, which used Ca(NO\textsubscript{3})\textsubscript{2}-based electrolytes as an example, driving the Ca-ion/sulfur–metal oxide driving the Ca-ion/sulfur–metal oxide window from the breakage of H-bonds, and thus an ultra-wide temperature window from \(-90\) to \(60^\circ\text{C}\).\textsuperscript{215} Xue et al. introduced super-concentrated sugars into 2 M NaNO\textsubscript{3} to reduce the free water molecules and destroy the tetrahedral structure, thus expanding the ESW to 2.812 V by breaking the hydrogen bonds. Consequently, LiBs, SiBs, PiBs and supercapacitors with excellent electrochemical performances were derived from the sugar-based electrolytes.\textsuperscript{216}

Briefly, salt-concentrated electrolytes can be a universal strategy to improve the energy density and cyclic stability and widen the working temperature windows of ARBs, which have been employed intensively and extensively, as summarized in Table 1 (both units of \(m\) and \(M\) were used herein, according to the different salt concentrations of various electrolytes).\textsuperscript{45,75–77,92,147,153,192,200–222} However, their cost probably impedes their large-scale applications because of the large amount of salt in these systems, although desirable performances have been obtained. The unit price of some representative salts utilized in salt-concentrated electrolytes is compared in Fig. 12, in which the corresponding information was collected from Sigma-Aldrich in USA, Sinoreagent in China and Alfa Aesar in the UK.\textsuperscript{190–192} It can be concluded from Fig. 12 that some organic salts are exceptionally expensive but only a little better in electrolyte performance than the cost-effective salts ranging from nitrites, perchlorates, and chlorates to acetates, and hence it is important for us to strike a balance between the properties of electrolytes and their cost in real applications.

### 3.4. Gelled electrolyte

Gelled aqueous electrolytes can be deemed as hydrogel electrolytes, consisting of a crosslinked network of polymer chains with interstitial spaces filled with solvent water, which endows the aqueous electrolyte with quasi-solid state and flexible property. Hydrogel electrolytes can be fabricated and applied in flexible and stretchable ARBs not only because of their physical properties but also highly available and tunable polymer chemistries. Hydrogel-based ARBs with self-healing property, shape memory and stretchability can enable the fabrication of wearable devices for health care, implantable devices, soft electronics, and strain sensors.\textsuperscript{107,223} The frequently used polymer host materials in hydrogel electrolytes include polyvinyl alcohol (PVA), PAA, PAM, gelatin, alginate, agarose, chitosan, poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) (PEO–PPO–PEO) and poly(N-isopropylacrylamide-co-acrylamide) (PNIPAM/AM), which possess various features, functional groups, crosslinking/gelation methods (Fig. 13a), and cooperate with aqueous solutions of different cations, anions and pH values.\textsuperscript{223}

#### 3.4.1. Minimizing water content for higher stability

The original function of hydrogel electrolytes based on their polymers was endowing ARBs with quasi-solid properties,\textsuperscript{224} while additional functions were also discovered to mitigate the challenges of ARBs. In a 5 M LiCl–PVA hydrogel electrolyte for supercapacitors, PVA could prevent the chemical dissolution of the V\textsubscript{2}O\textsubscript{5} electrode by minimizing the water content, providing a neutral pH medium, and serving as an elastic coating.\textsuperscript{225} With further development, PVA was found to further extend the ESW of an LiClO\textsubscript{4} aqueous solution, hence resulting in a higher energy density and cyclic stability in Zn–Li HiBs.\textsuperscript{226} By integrating PVA with the currently popular Wise (21 m LiTFSI), a flexible and wearable symmetrical ARLiB was developed with an energy density of 141 W h kg\textsuperscript{-1} during 4000 cycles using a single LiVPO\textsubscript{4}F as both the anode and cathode. In that cell, high energy and power density and flexibility were realized mutually in the presence of PVA.\textsuperscript{227} Besides PVA, carboxymethyl cellulose (CMC) was added to an acetate-based Wise (20 m KOAc) in a small amount (2 wt%) for gelling, which maintained a similar ESW as 32 m KOAc Wise with less salt dissolved. The existence of CMC reduced the dissolution of Mn and Fe in the KMHCF cathode, and then enhanced the cyclic stability of this PiB to 400 cycles.\textsuperscript{212} In 2020, a significant work was reported by Lu’s group using LiTFSI salt and poly(ethylene glycol) (PEG) polymer based on the common phenomenon of molecular crowding in living cells, which changed the hydrogen-bonding structure in water molecules, and thus reduced the activity of the water solvent. This molecular crowding electrolyte was optimized to 2 m LiTFSI–94% PEG–6% H\textsubscript{2}O\textsubscript{2}, delivering an ESW of 3.2 V and especially excellent stability against the HER (Fig. 13b), which endowed the Li\textsubscript{1}Ti\textsubscript{3}O\textsubscript{12}/LiMnO\textsubscript{2} full cell with an energy density ranging from 75 to 110 W h kg\textsuperscript{-1} over 300 charge–discharge cycles (Fig. 13c).\textsuperscript{228} Another similar work was reported in 2021 as a “water-in-gel” electrolyte, which consisted of water, NaCl, ZnCl\textsubscript{2} and sodium alginate (SA), expanding the ESW to 2.72 V. A “passway” for cation transportation was built within that electrolyte through coordinate bonds between the carboxylate groups of SA and Na/Zn ions. Also, due to the random coil conformation of the alginate chains, which was affected by dissolved ions, the 3D-fibrilar, porous polymer network ensured the uniform
Table 1  A summary of recent representative works on salt-concentrated electrolytes for ARBs

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Electrode</th>
<th>ESW (V)</th>
<th>Energy density (W h kg⁻¹)</th>
<th>Cyclic stability</th>
<th>Working temperature</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNO₃-2.5H₂O</td>
<td>AC/LiMnO₂ or LiNi₀.5Mn₀.5O₂</td>
<td>2.55</td>
<td>n/a</td>
<td>n/a</td>
<td>RT</td>
<td>213</td>
</tr>
<tr>
<td>8.37 m Ca(NO₃)₂-PVA</td>
<td>S/C/CA₉MnO₂</td>
<td>2.6</td>
<td>110</td>
<td>(total electrode)</td>
<td>150 cycles (0.2C)</td>
<td>RT</td>
</tr>
<tr>
<td>2 M NaNO₃ + 66.7 wt% sucrose</td>
<td>AC/PBA</td>
<td>2.8</td>
<td>n/a</td>
<td>n/a</td>
<td>RT</td>
<td>216</td>
</tr>
<tr>
<td>7.5 m ZnCl₂</td>
<td>Zn/polyaniline</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>RT</td>
<td>215</td>
</tr>
<tr>
<td>ZnCl₂ 0.03KBr·2H₂O</td>
<td>Zn/graphite</td>
<td>n/a</td>
<td>~440</td>
<td>(cathode)</td>
<td>100 cycles (0.25 A g⁻¹)</td>
<td>RT</td>
</tr>
<tr>
<td>30 m ZnCl₂</td>
<td>Zn symmetrical cell</td>
<td>2.3</td>
<td>n/a</td>
<td>600 hours</td>
<td>RT</td>
<td>207</td>
</tr>
<tr>
<td>30 m ZnCl₂</td>
<td>Zn-O/PVA</td>
<td>2.3</td>
<td>n/a</td>
<td>2000 cycles (5C)</td>
<td>RT</td>
<td>153</td>
</tr>
<tr>
<td>30 m KOAc</td>
<td>Zn-O/PVA</td>
<td>3.2</td>
<td>n/a</td>
<td>100 cycles (0.1 A g⁻¹)</td>
<td>30 °C</td>
<td>211</td>
</tr>
<tr>
<td>8 m LiOAc + 32 m KOAc</td>
<td>TiO₂/LiMnO₄</td>
<td>~3.0</td>
<td>n/a</td>
<td>11 000 cycles (1 A g⁻¹)</td>
<td>RT</td>
<td>205</td>
</tr>
<tr>
<td>7 m LiOAc + 45 m CsOAc</td>
<td>VOₓ/LiNi₀.5Mn₀.5O₄</td>
<td>~3.0</td>
<td>114.8</td>
<td>(total electrode)</td>
<td>1200 cycles (4C)</td>
<td>RT</td>
</tr>
<tr>
<td>1 m Zn(OAc)₂ + 31 m KOAc</td>
<td>Zn/MnO₂</td>
<td>3.1</td>
<td>232.7</td>
<td>(activated electrode and electrolyte)</td>
<td>600 cycles (C/3)</td>
<td>RT</td>
</tr>
<tr>
<td>4 M KOH + 16 M KOAc</td>
<td>Zn alloy/MnO₂@Ag</td>
<td>2.2</td>
<td>436.1</td>
<td>(activated electrode and electrolyte)</td>
<td>2300 min (~30 cycles, 25 mA cm⁻²)</td>
<td>RT</td>
</tr>
<tr>
<td>17 m NaClO₄</td>
<td>NaTi₂[P₂O₇]₄/NaN₃</td>
<td>2.7</td>
<td>36</td>
<td>(total electrode)</td>
<td>&gt;200 cycles (1C)</td>
<td>RT</td>
</tr>
<tr>
<td>21 m LiTFSI</td>
<td>Mo₅S₃O /[LiMnO₄]</td>
<td>~3.0</td>
<td>84</td>
<td>(total electrode)</td>
<td>1000 cycles (4.5C)</td>
<td>RT</td>
</tr>
<tr>
<td>21 m LiTFSI</td>
<td>LICGC/Li/RuTiS₂</td>
<td>~3.0</td>
<td>n/a</td>
<td>300 cycles (0.05 A g⁻¹)</td>
<td>RT</td>
<td>200</td>
</tr>
<tr>
<td>9.26 m NaOTf</td>
<td>NaTi₂[P₂O₇]₄/[Na₈.66[Mn₉₆,Ti₂₆]O₃₂]</td>
<td>2.5</td>
<td>31</td>
<td>(total electrode)</td>
<td>&gt;1200 cycles (1C)</td>
<td>RT</td>
</tr>
<tr>
<td>22 m KFSI</td>
<td>PTCDI/KFeMnHCF-3565</td>
<td>~3.0</td>
<td>80</td>
<td>(activated electrode and electrolyte)</td>
<td>10 000 cycles (100C)</td>
<td>~20 °C to 60 °C</td>
</tr>
<tr>
<td>3 M ZnFSI</td>
<td>Zn/ZnMnO₂</td>
<td>n/a</td>
<td>~202</td>
<td>(total electrode)</td>
<td>500 cycles (0.5 A g⁻¹)</td>
<td>RT</td>
</tr>
<tr>
<td>21 m LiTFSI + 7 m LiOTf</td>
<td>C/TiO₂/LiMnO₄</td>
<td>~3.1</td>
<td>100</td>
<td>(total electrode)</td>
<td>100 cycles (0.5C)</td>
<td>RT</td>
</tr>
<tr>
<td>21 m LiTFSI + 7 m LiOTf</td>
<td>passivated graphite/Li/Bi₂S₃/graphite</td>
<td>~3.1</td>
<td>460</td>
<td>(total electrode)</td>
<td>~250 cycles (0.08 A g⁻¹)</td>
<td>RT</td>
</tr>
<tr>
<td>21 m LiTFSI + 7 m LiOTf</td>
<td>S-KB/[LiMnO₃ or LiCoO₂]</td>
<td>~3.1</td>
<td>200</td>
<td>(total electrode)</td>
<td>&gt;1000 cycles (1C)</td>
<td>RT</td>
</tr>
<tr>
<td>21 m LiTFSI + 7 m LiOTf (open battery configuration)</td>
<td>Al₂O₃@LiTi₂[P₂O₇]₄ // LiMnO₄</td>
<td>~3.1</td>
<td>170</td>
<td>(total electrode)</td>
<td>1000 cycles (5C)</td>
<td>RT</td>
</tr>
<tr>
<td>42 m LiTFSI + 21 m Me₂EtN/TFSI</td>
<td>Li₂Ti₂O₇ // LiMnO₄</td>
<td>3.25</td>
<td>145</td>
<td>(total electrode)</td>
<td>150 cycles (0.2C)</td>
<td>RT</td>
</tr>
<tr>
<td>1 m Zn[TiF₄]₂ + 20 m LiTFSI</td>
<td>Zn/LiMnO₄</td>
<td>n/a</td>
<td>180</td>
<td>(total electrode)</td>
<td>4000 cycles (4C)</td>
<td>RT</td>
</tr>
<tr>
<td>1 m Zn[TiF₄]₂ + 20 m LiTFSI</td>
<td>Zn/Super P</td>
<td>n/a</td>
<td>300</td>
<td>(total electrode)</td>
<td>200 cycles (0.05 A g⁻¹)</td>
<td>RT</td>
</tr>
<tr>
<td>9 m NaOTf + 22 m TEAOTF</td>
<td>NaTi₂[P₂O₇]₄/[Na₈.66[V₂O₇]₄]</td>
<td>n/a</td>
<td>100 cycles (1C)</td>
<td>RT</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>25 m NaFSI + 10 m NaTFSI</td>
<td>NaTi₂[P₂O₇]₄/[Na₈.66[VOPO₄]₄]</td>
<td>2.7</td>
<td>64</td>
<td>(total electrode)</td>
<td>500 cycles (C/5, 1C)</td>
<td>~10 °C, 10 °C, 30 °C</td>
</tr>
<tr>
<td>Li[TiF₄]₂·(BETI)ₙ·2H₂O</td>
<td>Li₂Ti₂O₇ // LiNi₀.5Mn₀.5O₂</td>
<td>3.8</td>
<td>&gt;120</td>
<td>(total electrode)</td>
<td>100 cycles (6.8C)</td>
<td>RT</td>
</tr>
<tr>
<td>Na(TPTF)₂·(PFTS)(ₜ)₂·(OTF)₂·3·H₂O</td>
<td>NaTi₂[P₂O₇]₄/[Na₈.66[V₂O₇]₄]</td>
<td>2.7</td>
<td>77.9</td>
<td>(total electrode)</td>
<td>500 cycles (5C)</td>
<td>RT</td>
</tr>
<tr>
<td>Li[TiF₄]₂·(BETI)ₙ·2H₂O</td>
<td>LiSICON/Li/KB</td>
<td>3.8</td>
<td>950</td>
<td>(activated electrode and electrolyte)</td>
<td>50 cycles (0.5 A g⁻¹)</td>
<td>RT</td>
</tr>
<tr>
<td>Zn(ClO₄)₂·6H₂O–succinonitrile</td>
<td>Zn/poly(2,3-dithiin-1,4-benzoquinone)</td>
<td>2.55</td>
<td>n/a</td>
<td>3500 cycles (0.3C)</td>
<td>~20 °C, ~10 °C, RT</td>
<td>222</td>
</tr>
</tbody>
</table>

distribution and efficient transportation of Na/Zn ions in an aqueous environment. A Zn–Na hybrid battery based on this electrolyte was proposed, achieving a high extraction voltage of Na ions (2.1 V vs. Zn/Zn²⁺) and high capacity retention of 96.8% after 450 cycles.229

3.4.2. Lowering fluidity for higher energy density. Besides wide ESWs, the quasi-solid state and poor fluidity of hydrogel electrolytes also contribute to the high energy density of ARBs based on their decoupling structure. As noted above, a PAA-based alkaline hydrogel and PAM-cellulose-based acid hydrogel were prepared as a two-pH decoupling electrolyte, enabling a high working voltage in a Zn/MnO₂ battery (2.7 V), and thus high energy density. Compared with liquid decoupling electrolytes, hydrogel-based electrolytes simplify the three-chamber into a two-chamber structure, thus improving the relevant processibility.195 A gelled decoupling electrolyte with gelatin/ZnSO₄ analyte, gelatin/CuSO₄ catholyte, and anion-exchange separator was proposed, in which decoupling charge...
Fig. 12 Comparison of the unit price of various representative salts utilized in salt-concentrated electrolytes.

Fig. 13 (a) Molecular structure of frequently used polymer host materials for hydrogel electrolytes. (b) Comparison of ESWs between molecular crowding electrolyte and other salt-concentrated electrolytes. (c) Cyclic stability and CE of Li$_4$Ti$_5$O$_12$/LiMn$_2$O$_4$ cell based on molecular crowding electrolyte under 1C rate. (d) Schematic diagram of electrostatic interaction between anionic and cationic groups without salts, and proposed Li$^+$ migration mechanism in zwitterionic polymer hydrogel electrolyte.
carriers of anolyte and catholyte simultaneously endowed the Zn anode and S cathode with optimal redox chemistry, as follows:†\[230

Cathode: S + 2Cu^{2+} + 4e^{-} \leftrightarrow Cu_2S \quad (22)

Anode: Zn \leftrightarrow Zn^{2+} + 2e^{-} \quad (23)

Derived from this, the theoretical volumetric energy density of this flexible HiB was regarded as 3868 Wh L^{-1}, while the battery delivered a stable output voltage (released 92% of its full capacity within a small voltage drop of 0.15 V) and an ultrahigh reversible capacity of 2063 mAh g^{-1} (based on mass of S) under a current density of 100 mA g^{-1}.\[230

3.4.3. Anti-freezing for wider temperature window. Hydrogel electrolytes also possess anti-freezing function, which guarantees the stable operation of ARBs at low temperatures. A new type of zwitterionic polymer hydrogel electrolyte was fabricated, achieving high conductivity without sacrificing the flexibility of hydrogels at subzero temperatures. The anionic and cationic counterparts on the zwitterionic chains facilitated the dissociation of the LiCl salt, while the salt concentration significantly affected the conductivity and anti-freezing performance of the electrolytes. A direct hopping migration mechanism of hydrated Li+ through the channel of zwitterion groups was further proposed (Fig. 13d). The ultrahigh ionic conductivity of 12.6 mS cm^{-1} was achieved at -40 °C, owing to the synergistic effects including the electrostatic interactions between the zwitterionic groups and Li+ and the formation of an Li+(H2O)n hydration structure.\[231

Furthermore, a borax-crosslinked PVA/glycerol hydrogel electrolyte with a freezing point of below -60 °C was developed, in which glycerol could strongly interact with the PVA chains, thereby effectively prohibiting the formation of ice crystals in the whole gel network. This type of hydrogel electrolyte with 10.1 mS cm^{-1} at -35 °C, drove a Zn/MnO2 battery to charge/discharge for over 2000 cycles with around 90% capacity retention at that temperature.\[232 In summary, the performance of representative works is listed in Table S3 (ESI). To some extent, hydrogel electrolytes are a solvent strategy to solidify/inactivate water and achieve wider ESWs, higher stability, and a wider working temperature range, which are effective and economic for better ARBs. In next section, another method for solvent manipulation, named hybrid solvent, will be reviewed.

3.5. Hybrid-solvent electrolyte

The SEIs formed in LiSEs were found to be predominantly inorganic metal fluorides, originating from the reduction of salt anions of TFSI- or OTf-. However, the formation of this anion-originating SEI faces a severe “cathodic challenge” as result of the repulsion of anions by the negatively polarized anode surfaces, making the expansion of the cathodic limits extremely difficult.\[233,234 Therefore, a new class of electrolytes hybridizing aqueous and non-aqueous solvents was reported, which inherited the intrinsic merits of each system and successfully resolved the conflicts among performance, cost, interfacial chemistry, ambient control, and environmental concerns.

3.5.1. Hybridization with organic (aprotic) solvent. Dimethyl carbonate (DMC) was blended with an LiTFSI WiSE, introducing a secondary ingredient (alkylcarbamate) in the protective interphase on the anode in addition to LiF from anion reduction. This hybrid interphase, consisting of LiF and alkylicarbonate, stabilized the electrolyte down to 1.0 V vs. Li/Li+, allowing 3.2 V Li-ion cell chemistry of Li4Ti5O12 anode and LiNi0.5Mn1.5O4 cathode.\[233 Subsequently, the LiTFSI-DMC/water hybrid-solvent electrolyte was applied for DiBs, in which Li+ intercalation/deintercalation occurred on the Li4Ti5O12 side, while intercalation/deintercalation occurred on the graphite side.\[235 Furthermore, DMC was introduced in an LiTFSI + LiOTf WiBSE with both broad ESW and excellent safety, and assembled with a KS6 graphite cathode and Nb2O5 anode as DiB, which exhibited a good comprehensive performance including capacity, cycling stability, rate performance, and medium discharge voltage.\[236 Besides Li+-based chemistries, the hybrid solvent concept also suits SiBs. 7 m NaOTf aqueous solution was mixed with 8 m NaOTf propylene carbonate (PC) solution. Through Raman spectral characterization, intensified cation-anion association was observed in this electrolyte, which benefited the formation of an interphase at the electrode/electrolyte interface, thereby stabilizing the water molecules against the reducing surfaces of the electrodes. The Na+-based solvent-hybrid electrolyte offered an ESW of up to 2.8 V and enabled the NaTf2(PO4)2//Na2V2(PO4)3 redox pair.\[237

3.5.2. Hybridization with ionic liquid. The above-mentioned DMC and PC are regular organic solvents for conventional LiBs, while some ionic liquids were also mixed with aqueous solutions in some studies.\[238,239 Ionic liquids exhibit unique properties such as flame-retardant ability, non-volatility, and high thermal stability, but their high viscosity may hinder their further applications. Therefore, a “water in salt/ionic liquid” electrolyte composed of a salt of LiTFSI and a molten salt of 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide ([EMIM]-TFSI) was mixed with an extremely small amount of water (water/LiTFSI/EMIM-TFSI molar ratio of 1 : 1 : 2). In this electrolyte, the ESW was considerably widened without sacrificing the ionic conductivity, allowing accessibility to the full capacity of a commercial Nb2O5 material at a low potential window (-1.6 V vs. Ag/AgCl).\[239 Meanwhile, deep eutectic solvents (DESs), generally obtained by simply mixing Lewis acids and bases in a eutectic molar ratio, have emerged as attractive alternatives to ionic liquids due to their high degree of design freedom. 6 wt% water was added to a urea-based DES, endowing the Zn anode with unusual reversibility and durability. The intensified water-DES interactions significantly suppressed the water reactivity, while the merits of the aqueous system on the ionic conductivity and viscosity were conserved.\[238

3.5.3. Hybridization with low-freezing point solvent. Some organic solvents possessing low freezing points can be employed to enhance the low-temperature performance of ARBs by hybridizing aqueous electrolytes. For instance, the freezing point of acetonitrile (AN) is -48 °C, together with the properties of high dielectric constant (35.9), high oxidation stability (>5 V vs. Li/Li), and high miscibility with water, enabling an ARLiB with the Li4Ti5O12/LiMn2O4 redox pair to
Table 2  A summary of recent representative works on hybrid-solvent electrolytes for ARBs

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Electrode</th>
<th>ESW</th>
<th>Energy density</th>
<th>Cyclic stability</th>
<th>Working temperature</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>14 M LiTFSI in DMC/water</td>
<td>Li7Ti2O7//LiNiO2,Mn1/3O4</td>
<td>4.1 V</td>
<td>165 W h kg⁻¹</td>
<td>&gt;1000 cycles (6C)</td>
<td>RT</td>
<td>233</td>
</tr>
<tr>
<td>14 M LiTFSI in DMC/water</td>
<td>Li7Ti2O7//graphite</td>
<td>4.1 V</td>
<td>n/a</td>
<td>50 cycles (0.2 A g⁻¹)</td>
<td>RT</td>
<td>235</td>
</tr>
<tr>
<td>9.25 m LiTFSI + 3.1 LiOTF in DMC/water</td>
<td>Nb2O7/graphite</td>
<td>4.0 V</td>
<td>n/a</td>
<td>300 cycles (0.2 A g⁻¹)</td>
<td>RT</td>
<td>236</td>
</tr>
<tr>
<td>Li2(STEGDME)(H2O)2</td>
<td>Li7Ti2O7//LiMn2O4</td>
<td>4.2 V</td>
<td>120 W h kg⁻¹</td>
<td>500 cycles (3C)</td>
<td>RT</td>
<td>244</td>
</tr>
<tr>
<td>Mixture of 7 m NaOTf in water and 8 m NaOTf in PC LiTFSI + Zn(TFSI)2</td>
<td>Na7Li[(PO4)3//LiMn2O4</td>
<td>2.8 V</td>
<td>142.2 W h kg⁻¹</td>
<td>100 cycles (0.5C)</td>
<td>RT</td>
<td>245</td>
</tr>
<tr>
<td>LiTFSI/H2O(EMIM-TFSI)2,0</td>
<td>Li7Ti2O7//Na7V3(PO4)13</td>
<td>&gt;2.5 V</td>
<td>224.6 W h kg⁻¹</td>
<td>(cathode)</td>
<td>RT</td>
<td>237</td>
</tr>
<tr>
<td>15.3 m LiTFSI in AN/water Li7Ti2O7//LiMn2O4</td>
<td>Li7Ti2O7//LiMn2O4</td>
<td>4.5 V</td>
<td>45 W h kg⁻¹</td>
<td>600 cycles (0.1, 0.5, 1C)</td>
<td>RT</td>
<td>238</td>
</tr>
<tr>
<td>2 M ZnSO4 in EG/water Zn7+/PANI-V2O5</td>
<td>Zn7+/PANI-V2O5</td>
<td>2.8 V</td>
<td>51.9 W h kg⁻¹</td>
<td>3000 cycles (1 A g⁻¹)</td>
<td>RT</td>
<td>239</td>
</tr>
<tr>
<td>2 M ZnSO4 in Anti-M-50% V2O5</td>
<td>Zn7+/PANI</td>
<td>≈2.5 V</td>
<td>173 W h kg⁻¹</td>
<td>1000 cycles (5C)</td>
<td>RT, 0 °C</td>
<td>240</td>
</tr>
<tr>
<td>1.5 M LiI in DMF/water Zn7+/LiI</td>
<td>Zn7+/LiI</td>
<td>2.8 V</td>
<td>1700 W h kg⁻¹</td>
<td>&gt;250 cycles (0.2 A g⁻¹)</td>
<td>-40 °C to RT</td>
<td>241</td>
</tr>
</tbody>
</table>

exhibit high capacity at both RT and 0 °C.240 In addition, ethylene glycol (EG) has been widely used as antifreeze in engine coolant owing to its high boiling point and relatively low freezing point (−12 °C). When mixed with water, its freezing point can be further reduced (even to −40 °C), while the solvation interaction of Zn²⁺ with H₂O is partly reduced by the introduction of EG, contributing to fewer side reactions such as the HER on the Zn anode side. In a reported work by Li's group, the portion of EG in the mixture was optimized to 40% in volume, considering both ionic conductivity and ESW, which drove the Zn//PANI–V₂O₅ battery to more than 250 cycles under a current density of 0.2 A g⁻¹ at −20 °C.241 Qiao's group proposed a route using low-cost antisolvents, in which, for example, methanol was added to ZnSO₄ aqueous electrolyte to weaken the Zn²⁺ solvation sheath and minimize water activity by strengthening the interaction between the free and coordinated water molecules with antisolvents. The Zn reversibility was significantly boosted in the anisotropic electrolyte of 50% methanol in volume (anti-M-50%) at low or elevated temperatures. Based on the anti-M-50% electrolyte, the merits of the Zn//PANI coin cell/pouch cell were impressive, even repeatedly charged/discharged to 2000 cycles at −10 °C.242 Hydraziding solvents were also applied to ARFBs by Yu et al., who systematically studied a wide range of salts (LiCl, Li₂SO₄ and LiTFSI) and solvents (dimethoxyethane, DME; tetraethylene glycol dimethyl ether, TEGDME; acetonitrile, AN; and dimethylformamide, DMF). Finally, 1.5 M LiI in DMF/water was chosen because of its 2.8 V ESW and retained ionic conductivity at low temperatures, which enabled the successful operation of Zn//LiARFBs at −20 °C for 150 cycles with nearly no capacity loss.243 The merits of the works involving hybrid-solvent electrolytes are summarized (Table 2) based on representative papers in the literature.233,235–245 Also, depending on the merits, it can be concluded that the strategy of hydraziding solvents is promising if a balance among wide ESW, high ionic conductivity, low freezing point and cost can be found.

3.6. Electrode/current collector–electrolyte interface tuning

Interface tuning is a common strategy for all types of electrolytes, while the goals of tuning can be generally classified into thermodynamics (chemical and thermal stability) and kinetics (charge and mass transportation). Aqueous electrolytes possess superior interfacial kinetics and wettability, and thus it is more important to cover the shortage in thermodynamics. The SEI can kinetically stabilize electrolytes at potentials far beyond their thermodynamic stability limits, allowing cell reactions to proceed reversibly. However, it failed to occur in aqueous electrolytes until the discovery of WiSE. The formation mechanism of an SEI in WiSE are possibly contributed by two pathways, as follows: (1) reduction of anion complexes or clusters and (2) reduction of O₂ and CO₂ dissolved in the electrolyte (Fig. 14a),246 implied by combining various spectroscopic, electrochemical and computational techniques.

3.6.1. Solid electrolyte interface. The in situ constructed-SEI in WiSEs not only enabled a series of high voltage/energy density ARLiBs with unprecedented stability, but also brought high flexibility and even "open configurations", which have been hitherto unavailable for any LiBs chemistries.257,277,202 In contrast, in Zn²⁺-based aqueous systems, severe the HER during Zn plating/stripping makes the in situ formation of SEI impossible. As mentioned for the electrolyte additive strategy, some additives were added to facilitate the formation of an SEI in ARZiBs. Wang at el. used 0.5 m Me₃EtNOTf additive to build a fluorinated and hydrophobic interphase that conducts Zn²⁺, while suppressing the HER through the decomposition of alkylammonium ions.177 Meanwhile, the same group developed inorganic ZnF₂-Zn₅(CO₃)₂(OH)₆—organic bilayer SEI based on a low-concentration aqueous Zn(OTf)₂–Zn(NO₃)₂ electrolyte, mutually considering Zn²⁺ diffusion (inorganic...
inner layer) and water inactivation (organic outer layer). A \( \text{Zn}_2(\text{OH})_6(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O} \) layer was initially formed on the Zn anode surface via the self-terminated chemical reaction of \( \text{NO}_3^-/\text{C}_0 \) with \( \text{Zn}^{2+} \) and \( \text{OH}^-/\text{C}_0 \), and then it converted into \( \text{Zn}_2(\text{CO}_3)_2(\text{OH})_6 \), promoting the formation of \( \text{ZnF}_2 \) as the inner layer. Meanwhile, the organic-dominated outer layer was generated by the reduction of \( \text{OTf}^-/\text{C}_0 \).247

Another type of interfacial engineering is pre-coating an SEI/protective layer, which is more mechanically robust than and in situ-grown SEI. In the WISE system, a pre-coated anode-protected layer was prepared by adding 0.5 M LiTFSI and 10 wt% PEO to a mixture of 1,1,2,2-tetrafluoroethyl-2,2,2-trifluoroethyl ether (HFE) and DMC (95:5 in volume), vigorously heating and stirring at 75 \(^\circ\)C, which stabilized the graphite anode in a WiBSE and guaranteed a full cell with a working voltage of 4.0 V.248 The HFE–PEO protective gel was applied to another graphite anode in the same WiBSE, paired with the cathode of halogen conversion–intercalation chemistry, which not only provided a working voltage of more than 4.0 V but also considerably high capacity of 243 mA h g\(^{-1}\) (for total electrode mass).76 Besides ARLiBs, pre-coated protective layers were massively used on the surface of Zn metal anodes for the purpose of dendrite-control.249 A layer of sieve-element function (selective channel of \( \text{Zn}^{2+} \)) and uniform-pore distribution (\( \approx 3.0 \) nm) of a kaolin was prepared and coated on a Zn metal anode for alleviating dendrite and corrosion issues. Owing to the selective channel of \( \text{Zn}^{2+} \) and narrow distribution pore diameter of kaolin (Fig. 14b), homogeneous \( \text{Zn}^{2+} \) migration confined by this channel was achieved with dendrite-free deposition. Moreover, the coated kaolin (KL)–Zn anode exhibited long-time stability (800 h under current density of 1.1 mA h cm\(^{-2}\)), and accordingly suppressed side reactions at the anode surface/interface. This property was further verified by the KL-Zn//MnO\(_2\) cell with high initial specific capacity and good capacity retention and a reasonably well-preserved morphology, as characterized by SEM.250 A porous nano-CaCO\(_3\) coating was discovered to possess the ability to guide uniform and position-selected Zn stripping/plating at the nano-CaCO\(_3\)-layer/Zn metal anode interfaces. This Zn-deposition-guiding ability was mainly ascribed to the porous nature of the nano-CaCO\(_3\)-layer, considering the discovery of a similar functionality (even though relatively inferior) in Zn metal anodes coated with porous acetylene black or nano-SiO\(_2\) layers. The coated Zn anode was matched with a CNT–MnO\(_2\) cathode in ZnSO\(_4\) + MnSO\(_4\) electrolyte, showing a 42.7% higher discharge capacity than bare Zn metal anode (177 vs. 124 mA h g\(^{-1}\) at 1 A g\(^{-1}\)) after 1000 cycles.251

3.6.2. Cathode electrolyte interface. Compared with the SEI, the CEI has been rarely reported, but it is still worthy to be investigated and applied for improving the stability of the cathode–electrolyte interface against side reactions and cathode dissolution. One general strategy to construct a CEI

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**Fig. 14** (a) SEI formation mechanisms in WISE.246 (b) Schematic diagrams of Zn deposition process on bare Zn and KL–Zn with a detailed schematic diagram of confined \( \text{Zn}^{2+} \) transmission in kaolin.250 (c) Illustration of the in situ CEI layer strategy design.252 (d) Stability of Al and Ti current collectors in 15 m NaClO\(_4\) aqueous electrolyte.254 (e) Schematic illustration of eutectic strategy for dendrite and crack suppression.257
for suppressing the dissolution of vanadium-based cathodes in aqueous electrolytes and beyond was proposed, which introduced Sr ions into vanadium oxide layers as a sacrifice guest, leaching from the vanadium-based cathode as an in situ CEI coating layer on the surface (Fig. 14c). In ARLIBs, it is generally accepted that CEIs can only be formed in superconcentrated electrolytes containing fluorine-based organic anions (TFSI⁻, OTf⁻, etc.), while in a traditional nitrate-based aqueous electrolyte (pH-adjusted saturated LiNO₃), a CEI was initially discovered on the surface of the LiNO₃ cathode with the composition of Li₂CO₃ and LiOH, as demonstrated by transmission electron microscopy (TEM) and X-ray photoelectron (XPS). Under the protection of the CEI, the capacity retention of LiNO₃ was significantly enhanced in comparison of that in 1 M LiNO₃ + LiOH (pH = 10) aqueous electrolyte after 50 cycles.

3.6.3. Current collector. In the study regarding the HME of Li[TFSI]₀.₇(BETI)₀.₃·2H₂O, the effect from current collector to the ESW was confirmed, which could further understand the observed ESW when changing the cathode current collector to Ti and that of the anode into Al. Zhu et al. reported that oxidizing an Al current collector to Al₂O₃ (3 nm thickness surface) for the anode and Ti current collector to TiO₂ (5 nm thickness surface) for the cathode could expand the ESW of 15 M NaClO₄ aqueous electrolyte to 3.5 V (Fig. 14d). This wide ESW enabled the TiS₂ anode of SiBs to exhibit a low working potential (1.5 V vs. Na/Na⁺) for the first time. Thus, a full cell coupling a TiS₂ anode with PBA cathode in 15 M NaClO₄ aqueous electrolyte demonstrated a working voltage of 2.6 V and cyclic life up to 1000 times (30°C rate) with a high energy density of 100 W h kg⁻¹. In Zn metal anode-based ARBs, the substrates (current collectors) can also affect Zn stripping/plating. Archer’s group found that graphene with a low lattice mismatch for Zn was shown to be effective in driving the deposition of Zn with a locked crystallographic orientation relation. The resultant epitaxial Zn anodes achieved exceptional reversibility in 2 M ZnSO₄ aqueous electrolyte (10 000 cycles) and 1000 cycles of full-cell charging/discharging together with an α-MnO₂ cathode.

3.6.4. Electrode. In aqueous supercapacitor systems, tuning the electrode itself was also reported as a method to widen the ESW. In that work, the W atoms in the WO₃ crystal were partially replaced by Mo atoms, thus introducing oxygen vacancies. The negative limitation of the ESW was tunable as the WO₃ crystal ion-insulated crystallized salt, while the ESW was further expanded compared with that of the RTSGE due to the further compacted CIPs (Fig. 15c). Moreover, the stability window of the OSGE was still wide enough at elevated temperatures even after 50 cycles.

3.7. Beyond concentrated electrolyte

The benefits of salt-concentrated electrolytes towards ARBs have been intensively claimed here, while type kind of electrolyte has to use salts with high solubility, restricting its applications in scale and scope. Therefore, the routes concerning breaking the ceiling of salt solubility, thereby introducing more cost-effective salts with relatively low solubility, and further broadening ESW emerge, which can be classified into de-solvation/salting-out and solubility enhancement.

3.7.1. De-solvation. Zhou’s group developed a new liquid electrolyte for Li metal batteries with de-solvated Li⁺ (“Li⁺ de-solvated electrolyte”), which was merely composed of inactive “frozen-like” solvent and crystal-like salt solute. The addition of salts to the concentrated electrolytes could effectively eliminate the abundance of free solvents in the electrolytes and make the concentrated electrolytes more aggregative than their original counterparts. Specifically, the electrolyte configuration evolved from solvent-separated ion pair (SSIP)-dominated structures to contact ion pair (CIP)-dominated structures (Fig. 15a). This type of beyond concentrated electrolyte was even more aggregative than the saturated state and was composed of only crowded solvent-depleted CIPs without any free solvents. Tao’s group introduced this concept in aqueous electrolytes with inexpensive inorganic salts. An “oversaturated gel electrolyte” (OSGE) was simply prepared with PVA and saturated LiNO₃ at 95 °C. Subsequently, the excess salt was crystallized at room temperature, which was dispersed equally by the continuous room-temperature saturated gel (RTSG), forming a heterogeneous morphology (Fig. 15b). The continuous ion pathway ensured the considerable ionic conductivity of OSGE, regardless of the existence of ion-insulated crystallized salt, while the ESW was further expanded compared with that of the RTSGE due to the further compacted CIPs (Fig. 15c). Moreover, the stability window of the OSGE was still wide enough at elevated temperatures even at 80 °C, ensuring the desirable elevated temperature performance of ARLIBs. Meanwhile, a perchlorate OSGE (1 M Zn(ClO₄)₂ + 10 M LiClO₄-PVA) was also employed in Zn–Li HIBs by the same group, which showed an almost dendrite-free morphology with better cyclic stability. Yan et al. applied this strategy for the fabrication of electrolytes for low-temperature
Br to a further broadened ESW (Fig. 15g).220 The performance network of the WiHS electrolyte was severely disrupted, leading FTIR spectrum in Fig. 15f reveals that the hydrogen bonding inside this ice.262 which is attributed to the unique 3D ionic transport channels based on the asymmetric ammonium cation of Me3EtN+. The capacity of 605.7 mA h g−1 electrolyte drove a high-performance DiB to display a reversible which doubled the solubility of LiTFSI due to the inert salt 908.5 W h kg−1 (corresponding energy density of 908.5 W h kg−1).263 A 63 m “water-in-hybrid-salt” (WiHS) electrolyte (42 m LiTFSI + 21 m Me3EtN-TFSI) was prepared, which doubled the solubility of LiTFSI due to the inert salt based on the asymmetric ammonium cation of Me3EtN+. The FTIR spectrum in Fig. 15f reveals that the hydrogen bonding network of the WiHS electrolyte was severely disrupted, leading to a further broadened ESW (Fig. 15g).220 The performance of representative works is summarized in Table S5 (ESI†). Basically, the mechanism behind beyond concentrated electrolytes still needs more studies, especially more fundamental studies, although some excellent works about this electrolyte tuning strategy have been reported.

4. Future perspective and conclusions

Zn-ion capacitors, which possessed superior ionic conductivity (even $1.3 \times 10^{-3}$ S cm$^{-1}$ at $-60$ °C) based on Zn(ClO$_4$)$_2$ salty ice, which is attributed to the unique 3D ionic transport channels inside this ice.262

3.7.2. Increasing solubility. Beside de-solvation/salting-out, the solubility increasing route was also attempted. A ZnCl$_2$ + ZnBr$_2$ + Zn(OAc)$_2$ aqueous electrolyte with a record supersolvability of up to 75 m was reported, which broke through the physical solubility limit, owing to the formation of acetate-capped water–salt oligomers (WSOs) bridged by Br$^-$/Cl$^-$–H and Br$^-$/Cl$^-$/O–Zn$^{2+}$ interactions (Fig. 15d and e). This supersoluble electrolyte drove a high-performance DiB to display a reversible capacity of 605.7 mA h g$^{-1}$ (corresponding energy density of 908.5 W h kg$^{-1}$).263 At present, the salt-concentrated strategy is the most effective and efficient for high-energy and high-stability ARBs, whereas the cost of the salt is a challenge for large-scale applications. In the future, the hybrid solvent strategy can be more competitive if better non-aqueous solvents are discovered, which not only can reduce the cost, but also generate more stable electrode/electrolyte interfaces, thereby stabilizing ARBs. The artificial SEI/CEI can be another promising method; however, it is technically more difficult to create than hybrid solvents, and thus may take longer to be developed.

Despite the significant progress, there are still some potential challenges for the further commercialization of ARBs. Firstly, simulation and characterization towards aqueous electrolytes need to be improved. The parameters of MD simulation for the solvation sheath and DFT calculation for the electrode–electrolyte interface should be pre-set conscientiously rather than intentionally for supporting the as-obtained experimental results. In the case of the experimental characterization of the ion solvation structure, Raman, FTIR and NMR spectroscopy are used mostly as indirect methods, while seldom works have been reported using direct methods. X-ray nanoimaging was utilized for understanding the benefits of WISEs, which provided direct evidence for the stability of WiSEs compared with conventional aqueous electrolytes.265 However, that was
micron/sub-micron characterization, failing to approach the ion solvation sheath with a sub-nanosize. *In situ* liquid cell TEM was reported to reveal the nanoscale mineralization pathways of hydroxyapatite, which exhibits potential to characterize liquid aqueous electrolytes.\(^{266}\) Secondly, the necessity of high concentration should be reconsidered.\(^{267,268}\) For instance, in the ZnCl\(_2\) system, the concentration of 7.5 m rather than 30 m in the saturated state was selected as the optimum concentration for modulating the electrolyte structure, and thus suppressing the freezing of water.\(^{215}\) implying that, in some cases, too concentrated may be as bad as too diluted. Moreover, seawater can function as a desirable electrolyte for ARZiBs with a stable interfacial process through a Zn–Mn alloy anode,\(^{269}\) further demonstrating that suitable concentration and rational interfacial design are more critical than pursuing even more concentrated electrolytes. Further, Tarascon *et al.* indicated that there was still a long way to apply WiSEs, the most popular salt-concentrated species, because of their fragile *in situ*-grown SEI and poor elevated-temperature performances.\(^{270}\) The most evident benefit induced by salt-concentrated electrolytes is their expanded ESWs, and thus higher energy density of ARBs by pairing with high-working voltage electrodes. However, the electrode kinetics and mass transportation in salt-concentrated systems are usually undesirable due to their high viscosity and sluggish interfacial process. Nanosized electrodes can be an effective way to overcome kinetic issues, which balance the wide ESWs of the electrolyte and high capacity of the electrode when utilized in salt-concentrated electrolytes.\(^{92,212,261}\) Besides their relatively low working voltage, ZABs and ARFBs are regarded as effective aqueous chemistries to significantly improve the energy density through their dramatically enhanced capacity, which are promising alternatives for the salt-concentrated strategy. To some extent, ZABs and ARFBs are suitable substitutes for LiBs owing to both their high energy density and excellent safety,\(^{159,160,271}\) which are equally important in the future. The last issue is the gap between industry and academicians. In fact, reporting the performance based on a limited number of metrics does not give a realistic picture of the battery performance required for practical use. Although it is not necessary to force the standardization of the electrode and button cell design for fundamental research, it is of paramount importance to understand the influence of button cell design, fabrication, and testing protocol on the tested results, providing more reliable results as guidelines for future studies and applications.\(^{272,273}\) For real applications, the issue of self-discharge in ARBs should not be neglected, which is not only induced by macroscopical and microcosmic short circuit and electrode dissolution, but also direct chemical reactions (corrosion) between the electrode and electrolyte, especially for Zn foil electrodes. The reported long cyclic life of Zn metal-based batteries is normally obtained by testing a button cell immediately, neglecting the aging effects. Using Zn foil as both the working electrode and current collector will cause many problems when the battery is scaled up. Therefore, it is necessary to build up a Zn powder/current collector configuration with a longer calendar life.\(^{274}\) As mentioned above, ZABs and ARFBs with high capacity (high energy density) are promising for large-scale energy storage. Among the ARFBs, Zn//Br\(_2\) and Zn//I\(_2\) batteries are kinetically better than the Fe//Cr battery, while Zn corrosion is obstructive together with the corrosion of ARFBs. In the case of ZABs, besides the issues with the Zn metal anode, the sluggish kinetics of the ORR/OER at the cathode side also results in large polarization and low energy efficiency. The introduction of light has been demonstrated to boost the reaction kinetics of the ORR/OER, leading to enhanced electrochemical performances.\(^{275}\) Therefore, the synergic effect of electricity and light can cultivate thermodynamically and kinetically better ZABs, if the theoretical understanding of the photoelectrochemical process at oxygen cathodes is deeper, whilst relevant characterization technology becomes more advanced. Overall, aqueous energy storage systems have been extensively investigated through the development of novel electrolyte concepts, while there are still challenges to be tackled before their large-scale applications.

### Conflicts of interest

There are no conflicts to declare.

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### Notes and references


