



Recent Progress in “Water-in-Salt” Electrolytes Toward Non-lithium Based Rechargeable Batteries

Yuyan Wang, Xiaotang Meng, Jinfeng Sun, Yang Liu and Linrui Hou*

School of Materials Science & Engineering, University of Jinan, Jinan, China

Aqueous non-lithium based rechargeable batteries are emerging as promising energy storage devices thanks to their attractive rate capacities, long-cycle life, high safety, low cost, environmental-friendliness, and easy assembly conditions. However, the aqueous electrolytes with high ionic conductivity are always restricted by their intrinsically narrow electrochemical window. Encouragingly, the highly concentrated “water-in-salt” (WIS) electrolytes can efficiently expand the stable operation window, which brings up a series of aqueous high-voltage rechargeable batteries. In the mini review, we summarize the latest progress and contributions of various aqueous electrolytes for non-lithium (Na^+ , K^+ , Zn^{2+} , Mg^{2+} , and Al^{3+}) based rechargeable batteries, and give a brief exploration of the operating mechanisms of WIS electrolytes in expanding electrochemically stable windows. Challenges and prospects are also proposed for WIS electrolytes toward aqueous non-lithium rechargeable metal ion batteries.

OPEN ACCESS

Edited by:

Kwun Nam Hui,
University of Macau, China

Reviewed by:

Manickam Minakshi,
Murdoch University, Australia
Yan Huang,
Harbin Institute of Technology, China

*Correspondence:

Linrui Hou
mse_houlr@ujn.edu.cn

Specialty section:

This article was submitted to
Electrochemistry,
a section of the journal
Frontiers in Chemistry

Received: 18 March 2020

Accepted: 08 June 2020

Published: 07 August 2020

Citation:

Wang Y, Meng X, Sun J, Liu Y and
Hou L (2020) Recent Progress in
“Water-in-Salt” Electrolytes Toward
Non-lithium Based Rechargeable
Batteries. *Front. Chem.* 8:595.
doi: 10.3389/fchem.2020.00595

Keywords: “water-in-salt” electrolytes, aqueous batteries, non-lithium, rechargeable metal ion batteries, high energy density

INTRODUCTION

Recently, the safety issues and production costs of rechargeable batteries become the main factors restricting their commercial applications in portable electronic devices (PED), electrical vehicles (EV), and stationary electronic energy storage systems (EESs) (Wang et al., 2007; Suo et al., 2015; Lukatskaya et al., 2018). Thus, how to effectively select appropriate materials involved in batteries has become an important and challenging topic. As an important component of batteries, the electrolytes play a vital role in the superior electrochemical performance of batteries, and have attracted more and more attention in recent years (Kandhasamy et al., 2012; Yan et al., 2012; Suo et al., 2013). Although traditional organic electrolytes have exhibited appealing applications in rechargeable batteries, they inherently contain a large amount of expensive yet flammable organic solvents with certain levels of toxicity, which makes the device assembly conditions relatively harsh (Wang et al., 2012; Xu and Wang, 2016; Yang et al., 2019a). Consequently, aqueous electrolytes have been established as promising alternative candidates for advanced rechargeable batteries since their first application in lithium ion batteries (LIBs) (Li et al., 1994). The aqueous batteries display distinct merits, including low cost, high safety, high electronic conductivity, mild assembly environment, and so on (Wang et al., 2007; Baskar et al., 2014; Huang et al., 2019a). However, the electrochemical stability voltage window of aqueous batteries is as narrow as ~ 1.23 V, which seriously restricts the optimal choice of cathode and anode materials due to the existence of hydrogen and/or oxygen evolution reactions. This excludes most electrochemical couples that occur above the output voltage of 1.5 V, which limits the enhancement in energy density of full devices (Lu et al., 2011; Kim et al., 2014; Jiang et al., 2019a; Liu et al., 2020).

Recently, highly concentrated "water-in-salt" (WIS) electrolytes, in which the dissolved salts far outnumber the water molecules (salt/solvent ratio > 1 by volume or weight), have been reported to expand the stable voltage window up to ~3.0 V (Suo et al., 2016, 2017). In the WIS electrolytes, all water molecules participate in the ion solvation shells, and no "free" water remainders can be found. As a typical system, Suo et al. first developed a high concentration electrolyte with 21 m (mol kg⁻¹) of lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) for aqueous rechargeable LIBs (the molar ratio of Li⁺ to H₂O is 2.5) (Wang et al., 2015). However, the economic and environmental concerns, as well as the rarity and increasing consumption of Li resources, restrain the scalable applications of lithium-based electrochemical devices. As a consequence, the development of alternative aqueous rechargeable batteries based on some other earth-abundant elements turns out to be urgent and more meaningful. Therefore, the monovalent (Na⁺, K⁺) and/or multivalent (Zn²⁺, Mg²⁺, and Al³⁺) cation based aqueous secondary batteries have been intensively explored recently (Wessells et al., 2011; Zhao et al., 2016; Suo et al., 2017; Wang et al., 2020).

In this mini review, we mainly addressed the topic of the WIS electrolytes and their latest progress in various non-lithium aqueous rechargeable metal-ion batteries (ARMIBs). In the first section, we gave a brief exploration of the involved mechanism of WIS electrolytes in extending the electrochemical stability voltage window of devices. And then, we provided an extensive overview of the applications of WIS electrolytes in aqueous non-lithium secondary batteries, including aqueous sodium-ion batteries (ASIBs), aqueous potassium-ion batteries (APIBs), aqueous zinc-ion batteries (AZIBs), aqueous magnesium-ion batteries (AMIBs), and aqueous aluminum-ion batteries (AAIBs). Finally, we proposed the existing challenges and prospects for the future development of WIS electrolytes toward advanced non-lithium ARMIBs.

THE OPERATING MECHANISM OF "WIS" ELECTROLYTES IN EXTENDING THE ELECTROCHEMICAL WINDOW OF DEVICES

It is well-known that free water fraction is one of the key factors affecting the electrochemical stability of electrolytes (McEldrew et al., 2018; Vatamanu and Borodin, 2018). In traditional "salt-in-water" (SIW) electrolytes, the water molecules enormously outnumber the salts, and are relatively free to form hydrogen bonding networks. Thus, a large amount of water molecules will separate or solubilize (or corrode) the electrode material (Dubouis et al., 2018; Huang et al., 2019a). With the salt concentration increasing, the tighter solvation shell associated with WIS electrolytes can be formed. Meanwhile, the "freedom" water solvent molecules display a lower mobility. They turn out to be preferentially solvated by metal ions, and thus less available to separate salt anions. Accordingly, the water-water hydrogen bonds are replaced by water-ion-bonding interactions, enhancing the interactions between cations and anions, which

can further widen the stable working windows of electrolytes (Azov et al., 2018).

It is also believed that the formation of a solid electrolyte interphase (SEI) layer with a high salt concentration on the electrode surface can prevent water reduction, thus positively contributing to the wide electrochemical stability window. To be specific, the OH⁻ generated during the hydrogen oxygen reaction in the first cycle will chemically react with anions (such as TFSI) to mainly form a stable SEI film, which further prevents water reduction, and enhances the oxidative stability of the electrode masteries (Coustan et al., 2018; Dubouis et al., 2018). A typical solvation structure for WIS electrolytes is schematically depicted in **Scheme 1**.

It is well-known that it is an effective strategy to increase the energy density of batteries by raising the operating voltage (Xia et al., 2017; Manalastas et al., 2018). The voltage, according to the following Nernst equation, is highly dependent upon the half-cell potentials of both positive and negative electrodes.

$$\Delta V = V_+ - V_- \quad (1)$$

$$V = V^0 - \frac{RT}{nF} \ln \frac{C_{red}^a}{C_{ox}^b} \quad (2)$$

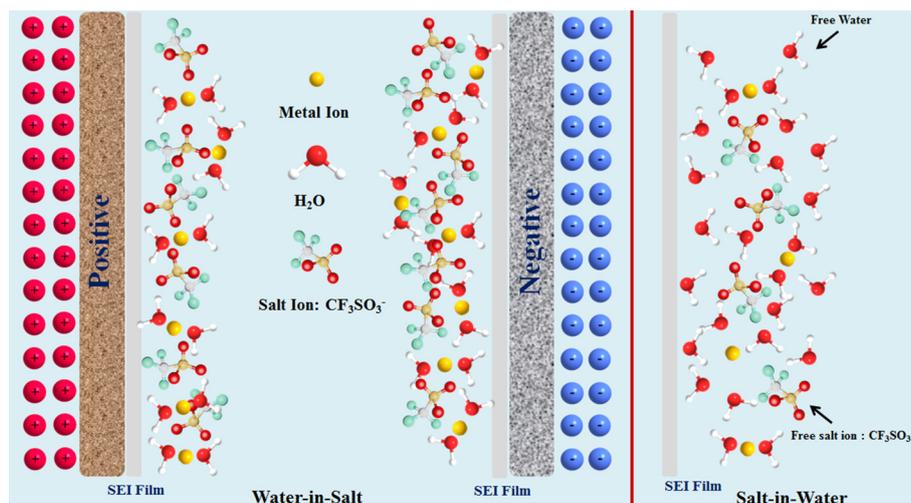
where V^0 is the standard half-cell reduction potential in respect to the standard hydrogen electrode (SHE), R is the universal gas constant, T is the absolute temperature in kelvins, n is the stoichiometric number of electrons, F is Faraday's constant, C_{red} is the concentration of the reduced form, C_{ox} is the concentration of the oxidized form, and a and b are exponential powers determined by the coefficients of C_{red} and C_{ox} in the redox half-reaction, respectively.

The maximum cell potential (ΔV) is critically determined by the potential subtraction between positive and negative ($V^0_+ - V^0_-$). The higher concentration of the oxidized form (C_{ox}) establishes stronger reduction potentials, as shown in Equations 1, 2. The electrolyte concentration and SEI film can effectively control the electrolyte decomposition, which allows even higher-concentration redox ions to participate in electrochemical reactions within the broadened electrochemical voltage window. Density functional theory (DFT) calculations are reported as an effective way to calculate reduction potentials of the anions' salts (Suo et al., 2015; Dawut et al., 2019; Shin et al., 2019).

WIS ELECTROLYTES FOR NON-LITHIUM ARMIBS

Considering some retrieved reviews about WIS electrolytes in lithium-based aqueous batteries (Wang et al., 2012; Kim et al., 2014), this mini-review will mainly focus on the latest progress in highly concentrated WIS electrolytes for non-lithium ARMIBs including ASIBs, APIBs, AZIBs, AMIBs, and AAIBs. The electrochemical properties of these batteries are systematically collected in **Table 1**.

It is well-known that electrolytes as ionic transport intermediates, with their inherent ionic conductivity, mobility, interfacial characteristics, and other properties, play a critical role



SCHEME 1 | Schematic diagram of the solvation structure for WIS electrolytes. By Linrui Hou, et al.

in enhancing the cycle performances. Designing and optimizing a functional electrolyte with a stable electrode/electrolyte interfaces has to be considered as an essential way to achieve a superior electrochemical performance in aqueous batteries. The typical design strategies are optimized by varying the electrolyte components, including salts and additives (Peng et al., 2017; Zhao et al., 2020).

The choice of salts significantly affects the electrochemical stability of the electrolytes, as well as their ionic conductivity and thermal stability. The salt anions in the aqueous WIS electrolytes can be commonly divided into inorganic (Cl^- , SO_4^{2-} , and ClO_4^-) and organic (CF_3SO_3^- , FSI^- , TFSI^- , BETI^- , and PTFSI^-) ones (Hong et al., 2013; Zhang et al., 2020). Inorganic salts are likely to be considered due to their low cost and high ionic conductivity. For instance, the fewer side reactions and low oxidation of Cl^- make it suitable for aqueous electrolytes (Zhang et al., 2018). In the case of SO_4^{2-} , the low cost, good compatibility, and exceptional stability make it more attractive; however, some by-products produced by over cycling still limits its practical application (Zhao et al., 2016; Huang et al., 2019b). Another anion is ClO_4^- , which has strong oxidability, lowering the potential for explosive risks and high toxicity (Lee et al., 2019). The bulky organic anions (i.e., CF_3SO_3^- , FSI^- , TFSI^- , BETI^- , and PTFSI^-) in aqueous electrolytes can reduce the solvation effect by occupying a large space. These anions show low ionic conductivity and corrosion issues (Yamada et al., 2016; Jiang et al., 2019a; Pan et al., 2019).

ASIBS

Sodium, as one an alkali metal, is closely located with lithium in the periodic table and has a relatively low electrochemical potential (-2.71 V vs. SHE). Typically, SIBs share many chemical properties with LIBs (Kim et al., 2012; Li et al., 2013; Boyd and Augustyn, 2018; Zheng et al., 2019). The high concentrated WIS electrolytes produce ASIBs with better cycling stability. However, the easy crystallization of highly concentrated electrolytes at

room temperature will seriously limit their practical application, and even damage the batteries (Wu et al., 2015; Reber et al., 2019; Zhang et al., 2020). Currently, the hydrate melts or bisalt, especially the adoption of asymmetric imide anions (such as FTFSI and PTFSI), are proved to be effective for reducing the viscosity and density as well as restraining crystallization by breaking the water structure and/or changing the probability of solvation structures with ion aggregations (Marcus, 2009; Brini et al., 2017; Suo et al., 2017), which thus results in the high solubility of salt anions (Suo et al., 2016; Zheng et al., 2019).

As reported in previous works, the commonly used salts in electrolytes of ASIBs are NaClO_4 , NaFSI , NaCF_3SO_3 (NaOTf), and NaTFSI due to their unique properties. Suo et al. first reported a Na^+ -conducting SEI layer on the surface of the $\text{NaTi}_2(\text{PO}_4)_3$ anode in an electrolyte of 9.26 m sodium trifluoromethane sulfonate (NaCF_3SO_3 or NaOTf), which expands the electrochemical stability window of $\text{NaTi}_2(\text{PO}_4)_3$ up to 2.5 V (vs. Na^+/Na) (Suo et al., 2017). Kühnel and co-workers obtained an ultra-high-concentration (up to 37 M) sodium bis(fluorosulfonyl)imide (NaFSI) in water by rapid solidification of the entire supersaturated solution, offering a stable electrochemical window of 2.6 V. Strikingly, an aqueous $\text{NaTi}_2(\text{PO}_4)_3//\text{Na}_3(\text{VOPO}_4)_2\text{F}$ sodium-ion battery with an electrolyte of 35 m NaFSI shows electrochemically reversible behaviors within an electrochemical window over 2.0 V (Kühnel et al., 2017). The NaFSI electrolytes with different concentrations are also shown to effectively broaden the voltage windows of ASIBs (Zheng et al., 2019). Another well-used electrolyte in ASIBs is NaClO_4 solution. When its molality increases to 17 m, a stable electrochemical potential window of ~ 2.8 V can be realized (Nakamoto et al., 2017, 2018; Lee et al., 2019). However, the potential explosive risk and high toxicity may hinder the extensive use of NaClO_4 . Battaglia et al. explored a $\text{NaTi}_2(\text{PO}_4)_3//\text{Na}_3(\text{VOPO}_4)_2\text{F}$ sodium-ion battery by employing the mixed $\text{NaFSI}/\text{NaFTFSI}$ electrolyte (25 m NaFSI and 10 m NaFTFSI). The unique device demonstrates

TABLE 1 | The main electrochemical properties for WIS-based aqueous non-lithium batteries.

Metal	Radius (nm)	Electrolytes	Voltage (V)	electrodes	References
Na	0.102	35 m NaFSI	2.6	NaTi ₂ (PO ₄) ₃ anode Na ₃ (VOPO ₄) ₂ F cathode	Kühnel et al., 2017
		18.5 m Na(PTFSI) _{0.65} (TFSI) _{0.14} (OTf) _{0.21} 3H ₂ O	2.7	Vs Na ⁺ /Na	Zheng et al., 2019
		Na(PTFSI) _{0.65} (TFSI) _{0.14} (OTf) _{0.21} 3H ₂ O	1.75	Na ₃ V ₂ (PO ₄) ₂ F ₃ NaTi ₂ (PO ₄) ₃ full cell	
		17m NaClO ₄	2.8	Na ₂ MnFe(CN) ₆ NaTi ₂ (PO ₄) ₃	Nakamoto et al., 2017
		17m NaClO ₄	2.7	Vs Na ⁺ /Na	Lee et al., 2019
		17m NaClO ₄	1.8	Na ₄ Fe ₃ (PO ₄) ₂ (P ₂ O ₇) NaTi ₂ (PO ₄) ₃ full-cell	
		25m NaFSI + 10m NaTFSI	1.9	Na ₃ (VOPO ₄) ₂ F NaTi ₂ (PO ₄) ₃ full-cell	Reber et al., 2019
K	0.138	9 m NaOTf + 22 m TEAOTf	3.3	Vs Ag/AgCl	Jiang et al., 2019a
		27.7 m K(PTFSI) _{0.12} (TFSI) _{0.08} (OTf) _{0.8} 2H ₂ O	2.5	vs K ⁺ /K	Zheng et al., 2019
		30 m KAc	3.2	KTi ₂ (PO ₄) ₃ as anode	Leonard et al., 2018
		22 m KCF ₃ SO ₃	3.0	vs Ag/AgCl	Jiang et al., 2019b
		22 m KCF ₃ SO ₃	2.6	KFeMnHCF-3565 PTCDI full cells	
Zn	0.074	30 m KFSI	3.97	vs. Hg/Hg ₂ Cl ₂)	Chen et al., 2020
		21 m LiTFSI + 0.5 m ZnSO ₄	1.8	LiMn _{0.8} Fe _{0.2} PO ₄ as cathode	Zhao et al., 2016
		21 m LiTFSI+ 1 m Zn(CF ₃ SO ₃) ₂	1.4	V ₂ O ₅ as anode	Hu et al., 2017
Al	0.0535	2.4 m KOH+1.0 m H ₂ SO ₄ acid-alkaline dual electrolyte	2.44	Zn/Zn(OH) ²⁻ -anode+ Mn ²⁺ /MnO ₂ as cathode	Liu et al., 2020
		5 m Al(CF ₃ SO ₃) ₃	2.65	PBA-type FeFe(CN) ₆ as cathode	Zhou et al., 2019
Mg	0.072	1 m MgSO ₄	1.5	PBN- Na _{1.4} Ni _{1.3} Fe(CN) ₆ 5H ₂ O polyimide full cells	Xia et al., 2017
		4 m Mg(TFSI) ₂	1.9	Li ₃ V ₂ (PO ₄) ₃ poly pyromellitic dianhydride	Wang et al., 2017

FSI, bis(fluorosulfonyl)imide; TFSI, bis(trifluoromethylsulfonyl)imide; OTf, trifluoromethane sulfonate; PTFSI, N(SO₂CF₃)(SO₂C₂F₅); TEA, tetraethylammonium; TFSI, bis(trifluoromethanesulfonyl)imide; PBN, Prussian blue; PTCDI, 3,4,9,10-perylenetetracarboxylic diimide.

superb electrochemical performance in terms of cycling stability, reversible capacity, and energy density within a wide operating temperature range from -10 to 30°C, benefiting from the positive role of the mixed electrolyte (Reber et al., 2019). A new type of mixed WIS electrolytes containing inert cations (TEA⁺) is prepared by dissolving sodium trifluoromethanesulfonate (NaOTf) and tetraethylammonium trifluoromethanesulfonate (TEAOTf) in water. When the total salt concentration is up to 31 m (9 m NaOTf and 22 m TEAOTf), the unique NaOTf/TEAOTf electrolyte is endowed with a wide voltage window of ~3.3 V, and suppresses the dissolution of the positive transition metal as well (Jiang et al., 2019a).

APIBS

Potassium-ion batteries (PIBs) are also considered to be a promising energy storage system due to their abundant potassium resources (Su et al., 2016; Eftekhari et al., 2017). Generally, potassium owns lower standard redox potential than its counterparts of Na and Li, which will guarantee PIBs with

a potentially higher cell voltage. However, the higher ionization potential and larger ionic radius of K itself have limited the choice of electrode materials for advanced APIBs (Suo et al., 2017; Hwang et al., 2018). Thanks to the smaller Stokes radius of solvated K⁺ owing to its weak Lewis acidity, and the low interfacial reaction resistance due to the small desolvation activation energy, the K-containing electrolytes always display higher conductivity than its Li/Na counterparts (Komaba et al., 2015; Kim et al., 2017; Chen et al., 2020). Meanwhile, the weak oxidation resistance of electrolytes and the insufficient passivation on the surface of negative electrodes leads to modest reversible capacities, especially at the initial cycle, or in the high-voltage (>4.0 V) operation windows, which limits the huge development of APIBs (Hosaka et al., 2018). Therefore, it is essential to fit the high energy APIBs to purposefully explore suitable electrolytes.

Leonard and co-workers first reported the aqueous electrolyte of 30 m potassium acetate (KAc) for APIBs (Leonard et al., 2018). With the electrolyte, the KTi₂(PO₄)₃ (KTP) anode displays

good reversible behaviors within an extended electrochemical window from -1.7 to 1.5 V (vs. Ag/AgCl). Compared to the KAc and LiTFSI-based electrolytes with the same concentration, the bis(fluorosulfonyl)imide(KFSI)-based electrolytes exhibit higher conductivity (Chen et al., 2020). The electrolyte of 30 m KFSI also displays an electrochemical stability window from -1.55 to 2.42 V (vs. Hg/Hg₂Cl₂), which enables the *b*-perylene-3,4,9,10-tetracarboxylic dianhydride (*b*-PTCDA), and even *b*-PTCDA-based full batteries to stably operate in such high-concentration electrolytes without hydrogen evolution and material dissolution (Chen et al., 2020). Jiang et al. also investigated an aqueous 3,4,9,10-perylenetetracarboxylic diimide (anode)//K_{1.85}Fe_{0.33}Mn_{0.67}[Fe(CN)₆]_{0.98}·0.77H₂O (cathode) full device with 20 m KCF₃SO₃ (KOTf) WIS electrolyte, and the full battery exhibits an unprecedented performance in terms of reversible capacities and rate behaviors (Jiang et al., 2019b).

The asymmetric hydrate melts with an optimized eutectic system have been reported as a stable aqueous electrolyte with good fluidity and reduced viscosity/density, in which all water molecules participate in Li⁺ hydration shells (Yamada et al., 2016). With the introduced stable asymmetric anion (i.e., PTFSI⁻), the K(PTFSI)_{0.12}(TFSI)_{0.08}(OTf)_{0.8}·2H₂O as the alkali melts exhibits excellent water solubility and an expanded operating window of ~ 2.5 V (~ 2.14 – 4.65 V vs. K⁺/K), but does not suffer from the vulnerable S-F bond. Moreover, the ionic conductivity of the K(PTFSI)_{0.12}(TFSI)_{0.08}(OTf)_{0.8}·2H₂O is maintained at ~ 34.6 mS cm⁻¹, much higher than other typical non-aqueous electrolytes (~ 10 mS cm⁻¹) (Zheng et al., 2019).

AZIBS

Recently, AZIBs, due to their remarkable thermal stability, high theoretical specific capacity (~ 820 mAh g⁻¹), intrinsic safety, and low cost of the Zn metal, are considered to be the most promising alternative to LIBs. Moreover, the metallic Zn is stable, and can be directly utilized as an electrochemically reversible anode in aqueous electrolytes (Zhang, 1996; Li et al., 2019). However, its extensive applications are still limited by suitable aqueous electrolytes with excellent thermal properties and safety. Previous works have shown that the alkaline aqueous electrolytes result in the formation of zinc dendrite and the by-product of ZnO, causing a poor cycle capacity and low CE values (Zhang et al., 2014; Wang et al., 2018a). Similarly, the Zn salts-based neutral or mildly acidic electrolytes with high concentrations are a very effective way to address these issues.

Typically, ZnSO₄ and Zn(CF₃SO₃)₂ solutions are commonly used electrolytes for AZIBs because of their excellent stability and compatibility (Song et al., 2018). Zhao et al. assembled a Zn//LiMn_{0.8}Fe_{0.2}PO₄ aqueous hybrid-ion battery with 0.5 m ZnSO₄ and 21 m LiTFSI as the WIS electrolyte. The unique device provides a high energy density of ~ 183 Wh kg⁻¹ and a high operating voltage exceeding 1.8 V (Zhao et al., 2016). However, the ZnSO₄ electrolyte for AZIBs always suffers from its intrinsically limited solubility and lower Zn stripping/plating efficiency. In contrast, the Zn(CF₃SO₃)₂ electrolyte exhibits smaller polarization and higher CE values, which makes it suitable for wide application in aqueous ZIBs (Huang et al., 2019b; Xie et al., 2020). Mai's group designed a novel Zn//V₂O₅

aqueous hybrid-ion battery with the WIS electrolyte of 1 m Zn(CF₃SO₃)₂ and 21 m LiTFSI. Compared to that with the Zn(CF₃SO₃)₂ (1 m), the Zn//V₂O₅ battery with the WIS-electrolyte (21 m LiTFSI and 1 m Zn(CF₃SO₃)₂) displayed a more stable charge/discharge plateau and cycling performance (Hu et al., 2017). Furthermore, owing to the large-size TFSI⁻ anions, the Zn(TFSI)₂, as a novel organic zinc salt can effectively reduce the solvation effect. Wang's group developed a WIS electrolyte of 1 m Zn(TFSI)₂ + 20 m LiTFSI, which is capable of retaining the water in an open atmosphere. It effectively promotes the dendrite-free plating/stripping of metallic Zn with nearly 100% CE and brings unprecedented reversibility to the aqueous ZIBs with either LiMn₂O₄ or O₂ cathodes (Wang et al., 2018a). Additionally, a new low-cost WIS electrolyte of 30 m ZnCl₂ can deliver a wide electrochemical window of 2.3 V due to its fewer side reactions and low oxidative Cl⁻ (Zhang et al., 2018). In the symmetric Zn||Zn cell with a 30 m ZnCl₂ electrolyte, the Zn electrode renders a high CE of 95.4% and a high stable galvanostatic charge-discharge profile of over 600 h without any significant overpotential fluctuation (Zhang et al., 2018).

AMIBS

Multivalent ions, as good transporters, can carry more electrons than monovalent ions. Besides the Zn²⁺, another bivalent metal ion of Mg²⁺ with low reduction potential (-2.37 V) is also considered as a predominant charge carrier for AMIBs due to the high volumetric specific capacity of Mg (~ 3833 mAh L⁻¹) and the total lack of dendrite growth (Rasul et al., 2012; Song et al., 2015; Xu et al., 2015; Sun et al., 2016). The current development and practical applications of the electrolytes for AMIBs are limited by the corrosion of the electrolytes (Wang et al., 2017; Zhao et al., 2020). The electrochemical Mg dissolution occurs at a high overpotential which restrains the selection of solvents (Hebié et al., 2017). Consequently, the commonly used anions (Cl⁻, SO₄²⁻, ClO₄⁻, CF₃SO₃⁻) in other AMIBs cannot be directly applied to AMIBs. Moreover, the high charge density of multivalent ions will induce strong coulombic interactions with both the lattice of electrolyte solvents and electrode materials, which is an adverse factor for improving electrochemical performance (Lapidus et al., 2014; Wang et al., 2018b). So far, the AMIBs are still in its infancy; only a few possible materials based on WIS electrolytes show reversible performance toward AMIBs.

Moreover, Mg(TFSI)₂, as a neutral molecule, is completely non-corrosive, safe, and green, and can be anticipated for AMIBs application (Yoo et al., 2013). Wang et al. fabricated a poly pyromellitic dianhydride//Li₃V₂(PO₄)₃ device by using 4 m Mg(TFSI)₂ as the electrolyte. The full cell exhibits superior electrochemical properties including an excellent rate capability, high power density, and high capacity retention in an electrochemical window of 1.9 V (Wang et al., 2017).

AAIBS

Aluminum is the first abundant metal element in the earth's crust, which has been investigated widely as the anode material for AAIBs (Wang et al., 2016). Moreover, the ion radius of Al³⁺ (0.054 nm) is much smaller than Li⁺ (0.076 nm),

which ensures the rapid insertion/extraction of Al^{3+} during the charge/discharge process (Rudd and Gibbons, 1994; Li et al., 2007; Das et al., 2017; Yang et al., 2019b). Furthermore, the Al anode possesses a large gravimetric/volumetric capacity ($\sim 2,980 \text{ mAh g}^{-1}/\sim 8,046 \text{ mAh cm}^{-3}$), due to its unique three-electron transfer capability. However, the low ionic conductivity, corrosion with low concentration electrolytes, and dendrites growth still limits the electrochemical stability of electrolytes, thereby limiting its large-scale energy applications (Liu et al., 2012; Nakayama et al., 2015; Zhao et al., 2018). So, the key for developing AAIBs is to exploit WIS electrolytes toward high-performance electrodes, which can enable the dissolution of dendrites, thereby significantly improve the cycling stability.

AlCl_3 , due to the ultra-low cost and safety, is widely used as the electrolytes for AAIBs. Pan et al. reported a high-concentration aqueous AlCl_3 solution (3.382 m) as the electrolyte for a novel Al/ AlCl_3 /graphite aqueous battery, which can stably operate within an electrochemical stability window of $\sim 4 \text{ V}$, and exhibit a large capacity of ~ 165 at 500 mA g^{-1} along with a high CE of 95% over 1,000 cycles (Pan et al., 2019). Additionally, the $\text{Al}(\text{OTf})_3$ is another type of electrolyte with a noncorrosive property, which makes it more favorable than corrosive AlCl_3 when applied in AAIBs (Das et al., 2017). Chen's group introduced the electrolyte of 5 m $\text{Al}(\text{OTf})_3$ for electrochemical evaluation of the Prussian Blue Analogs-type $\text{FeFe}(\text{CN})_6$ (FF-PBA) cathode. Appealingly, with the electrolyte, the FF-PBA shows an extraordinarily high initial discharge capacity of $\sim 116 \text{ mAh g}^{-1}$ and long cycle life with a capacity fading of 0.39% per cycle in the expanded operation window of 2.65 V (Zhou et al., 2019). Until now, there are few other WIS electrolytes reported for AAIBs.

CONCLUSION

Electrolytes, as ionic transport intermediates with inherent ionic conductivity, mobility, interfacial characteristics, and other properties, play a critical role in enhancing the cycle performances, rate capacity, and safety of batteries. WIS electrolytes with highly concentrated salt solutions specifically can expand electrochemical potential windows of aqueous devices up to about 3 V and result in low solvent (water molecules) activities and high chemical stabilities (restraining side reactions). Moreover, the formation of stable SEI film also endows the cells with a high energy density and excellent cycling stability. This mini review mainly focuses on the WIS electrolytes

REFERENCES

- Azov, V. A., Egorova, K. S., Seitkalieva, M. M., Kashin, A. S., and Ananikov, V. P. (2018). "Solvent-in-salt" systems for design of new materials in chemistry, biology and energy research. *Chem. Soc. Rev.* 47, 1250–1284. doi: 10.1039/c7cs00547d
- Baskar, S., Meyrick, D., Kalai Selvan, R., and Minakshi, M. (2014). Facile and large scale combustion synthesis of alpha- CoMoO_4 : Mimics the redox behavior of a battery in aqueous hybrid device. *Chem. Eng. J.* 253, 502–507. doi: 10.1016/j.cej.2014.05.068
- Boyd, S., and Augustyn, V. (2018). Transition metal oxides for aqueous sodium-ion electrochemical energy storage. *Inorg. Chem. Front.* 5, 999–1015. doi: 10.1039/c8qi00148k
- Brini, E., Fennell, C. J., Fernandez-Serra, M., Hribar-Lee, B., Lukšič, M., and Dill, K. A. (2017). How water's properties are encoded in its molecular structure and energies. *Chem. Rev.* 117, 12385–12414. doi: 10.1021/acs.chemrev.7b00259
- Chen, H., Zhang, Z. Y., Wei, Z. X., Chen, G., Yang, X., Wang, C. Z., et al. (2020). Use of a water-in-salt electrolyte to avoid organic material dissolution and enhance the kinetics of aqueous potassium ion batteries. *Sustain. Energy Fuels* 4, 128–131. doi: 10.1039/c9se00545e

for ARMIBs and summarizes the recent investigation of WIS electrolytes in non-lithium monovalent (Na, K) and multivalent (Zn, Mg, Al) ion batteries.

However, research based on the WIS electrolytes is still at the primary stage, according to the achievements reported so far; the challenges and prospects for the future development of WIS electrolytes toward non-lithium ARMIBs are proposed as follows. First, the scientific foundation for the highly concentrated WIS electrolytes will render some novel yet unknown concepts, which may be in conflict with current classic theories, and should be further unveiled with the elegant combination of *in/ex-situ* spectroscopic techniques and theoretical simulation/calculation. For instance, an in-depth understanding of intrinsic ionic transport and functional SEI formation mechanisms in the WIS electrolyte, which are distinct from the conventional SIW systems, should be comprehensively conducted. Second, further exploration of appropriate salts, particularly with high thermodynamic stability, super ionic conductivity, and good compatibility with both electrodes at a low cost, should also be taken into account for high-performance WIS electrolytes, considering their practical commercial applications. Third, the balance between high-concentration electrolytes and low viscosity and crystallization also needs to be solved.

Despite facing huge difficulties and challenges, we firmly believe that aqueous rechargeable batteries based on WIS electrolytes will receive rapid and sustained development in the near future. This will result in new avenues for the future energy storage landscape.

AUTHOR CONTRIBUTIONS

YW: formal analysis, investigation, writing—original draft, and writing—review & editing. XM: investigation. JS: formal analysis and writing—review & editing. YL: visualization and software. LH: formal analysis, investigation, conceptualization, writing—review & editing, and funding acquisition. All authors contributed to the article and approved the submitted version.

FUNDING

This work was supported by the National Natural Science Foundation of China (Nos. 51772131, 51802119), Natural Science Doctoral Foundation of Shandong Province (ZR2019BEM038, ZR2019BB057), and Natural Science Doctoral Foundation of the University of Jinan (XBS1830).

- Coustan, L., Zaghbi, K., and Bélanger, D. (2018). New insight in the electrochemical behaviour of stainless steel electrode in water-in-salt electrolyte. *J. Power Sources* 399, 299–303. doi: 10.1016/j.jpowsour.2018.07.114
- Das, S. K., Mahapatra, S., and Lahan, H. (2017). Aluminium-ion batteries: developments and challenges. *J. Mater. Chem. A* 5, 6347–6367. doi: 10.1039/c7ta00228a
- Dawut, G., Lu, Y., Miao, L. C., and Chen, J. (2019). High-performance rechargeable aqueous zn-ion batteries with poly(benzoquinonyl sulfide) cathode. *Inorg. Chem. Front.* 5, 1391–1396. doi: 10.1039/c8q00197a
- Dubouis, N., Lemaire, P., Mirvaux, B., Salager, E., Deschamps, M., and Grimaud, A. (2018). The role of hydrogen evolution reaction on the solid electrolyte interphase formation mechanism for "water-in-salt" electrolytes. *Energy Environ. Sci.* 11, 3491–3499. doi: 10.1039/c8ee02456a
- Eftekhari, A., Jian, Z. L., and Ji, X. (2017). Potassium secondary batteries. *ACS Appl. Mater. Interfaces* 9, 4404–4419. doi: 10.1021/acsmi.6b07989
- Hebié, S., Ngo, H. P. K., Leprêtre, J. C., Iojoiu, C., Cointeaux, L., Berthelot, R., et al. (2017). Electrolyte based on easily synthesized, low cost triphenolate-borohydride salt for high performance Mg(TFSI)₂-glyme rechargeable magnesium batteries. *ACS Appl. Mater. Interfaces* 9, 28377–28385. doi: 10.1021/acsmi.7b06022
- Hong, S. Y., Kim, Y., Park, Y., Choi, A., Choi, N., and Lee, K. T. (2013). Charge carriers in rechargeable batteries: Na ions vs. Li ions. *Energy Environ. Sci.* 6, 2067–2081. doi: 10.1039/c3ee40811f
- Hosaka, T., Kubota, K., Kojima, H., and Komaba, S. (2018). Highly concentrated electrolyte solutions for 4 V class potassium-ion batteries. *Chem. Comm.* 54, 8387–8390. doi: 10.1039/c8cc04433c
- Hu, P., Yan, M. Y., Zhu, T., Wang, X. P., Wei, X. J., Li, J. T., et al. (2017). Zn/V₂O₅ Aqueous hybrid-ion battery with high voltage platform and long cycle life. *ACS Appl. Mater. Interfaces* 9, 42717–42722. doi: 10.1021/acsmi.7b13110
- Huang, J. H., Guo, Z. W., Ma, Y. Y., Bin, D., Wang, Y. G., and Xia, Y. G. (2019a). Recent progress of rechargeable batteries using mild aqueous electrolytes. *Small Methods* 3:1800272. doi: 10.1002/smt.201800272
- Huang, S., Zhu, J. C., Tian, J. L., and Niu, Z. Q. (2019b). Recent progress in the electrolytes of aqueous zinc-ion batteries. *Chem. Eur. J.* 25, 1–16. doi: 10.1002/chem.201902660
- Hwang, J.-Y., Myung, S.-T., and Sun, Y.-K. (2018). Recent progress in rechargeable potassium batteries. *Adv. Fun. Mater.* 28:1802938. doi: 10.1002/adfm.201802938
- Jiang, L. W., Liu, L. L., Yue, J. M., Zhang, Q. Q., Zhou, A. X., Borodin, O., et al. (2019a). High-voltage aqueous Na-ion battery enabled by inert-cation-assisted water-in-salt electrolyte. *Adv. Mater.* 32:1904427. doi: 10.1002/adma.201904427
- Jiang, L. W., Lu, Y. X., Zhao, C. L., Liu, L. L., Zhang, J. N., Zhang, Q. Q., et al. (2019b). Building aqueous K-ion batteries for energy storage. *Nat. Energy* 4, 495–503. doi: 10.1038/s41560-019-0388-0
- Kandhasamy, S., Pandey, A., and Minakshi, M. (2012). Polyvinylpyrrolidone assisted sol-gel route LiCo_{1/3}Mn_{1/3}Ni_{1/3}PO₄ composite cathode for aqueous rechargeable battery. *Electrochim. Acta* 60, 170–176. doi: 10.1016/j.electacta.2011.11.028
- Kim, H., Hong, J., Park, K.-Y., Kim, H., Kim, S.-W., and Kang, K. (2014). Aqueous rechargeable Li and Na ion batteries. *Chem. Rev.* 114, 11788–11827. doi: 10.1021/cr500232y
- Kim, H., Kim, J. C., Bianchini, M., Seo, D.-H., Rodriguez-Garcia, J., and Ceder, G. (2017). Recent progress and perspective in electrode materials for K-ion batteries. *Adv. Energy Mater.* 8:1702384. doi: 10.1002/aenm.201702384
- Kim, S.-W., Seo, D.-H., Ma, X. H., Ceder, G., and Kang, K. (2012). Electrode materials for rechargeable sodium-ion batteries: potential alternatives to current lithium-ion batteries. *Adv. Energy Mater.* 2, 710–721. doi: 10.1002/aenm.201200026
- Komaba, S., Hasegawa, T., Dahbi, M., and Kubota, K. (2015). Potassium intercalation into graphite to realize high-voltage/high-power potassium-ion batteries and potassium-ion capacitors. *Electrochim. Commun.* 60, 172–175. doi: 10.1016/j.elecom.2015.09.002
- Kühnel, R. S., Reber, D., and Battaglia, C. (2017). A high-voltage aqueous electrolyte for sodium-ion batteries. *ACS Energy Lett.* 2, 2005–2006. doi: 10.1021/acsenerylett.7b00623
- Lapidus, S. H., Rajput, N. N., Qu, X., Chapman, K. W., Persson, K. A., and Chupas, P. J. (2014). Solvation structure and energetics of electrolytes for multivalent energy storage. *Phys. Chem. Chem. Phys.* 16, 21941–21945. doi: 10.1039/c4cp03015j
- Lee, M. H., Kim, S. J., Chang, D. H., Kim, J. S., Moon, S., Oh, K., et al. (2019). Toward a low-cost high-voltage sodium aqueous rechargeable battery. *Mater. Today* 29, 26–36. doi: 10.1016/j.mattod.2019.02.004
- Leonard, D. P., Wei, Z. X., Chen, G., Du, F., and Ji, X. L. (2018). Water-in-salt electrolyte for potassium-ion batteries. *ACS Energy Lett.* 3, 373–374. doi: 10.1021/acsenerylett.8b00009
- Li, C. S., Ji, W. Q., Chen, J., and Tao, Z. L. (2007). Metallic aluminum nanorods: synthesis via vapor-deposition and applications in Al/air batteries. *Chem. Mater.* 19, 5812–5814. doi: 10.1021/cm7018795
- Li, W., Dahn, J. R., and Wainwright, D. (1994). Rechargeable lithium batteries with aqueous electrolytes. *Science* 264, 1115–1118. doi: 10.1126/science.264.5162.1115
- Li, X. L., Ma, L. T., Zhao, Y. W., Yang, Q., Wang, D. H., Huang, Z. D., et al. (2019). Hydrated hybrid vanadium oxide nanowires as the superior cathode for aqueous Zn battery. *Mater. Today Energy* 14:100361. doi: 10.1016/j.mtener.2019.100361
- Li, Z., Young, D., Xiang, K., Carter, W. C., and Chiang, Y.-M. (2013). Towards high power high energy aqueous sodium-ion batteries: the NaTi₂(PO₄)₃/Na_{0.44}MnO₂ System. *Adv. Energy Mater.* 3, 290–294. doi: 10.1002/aenm.201200598
- Liu, C., Chi, X. W., Han, Q., and Liu, Y. (2020). A high energy density aqueous battery achieved by dual dissolution/deposition reactions separated in acid-alkaline electrolyte. *Adv. Energy Mater.* 10:1903589. doi: 10.1002/aenm.201903589
- Liu, S., Hu, J. J., Yan, N. F., Pan, G. L., Li, G. R., and Gao, X. P. (2012). Aluminum storage behavior of anatase TiO₂ nanotube arrays in aqueous solution for aluminum ion batteries. *Energy Environ. Sci.* 5, 9743–9746. doi: 10.1039/c2ee22987k
- Lu, Y. H., Goodenough, J. B., and Kim, Y. (2011). Aqueous cathode for next-generation alkali-ion batteries. *J. Am. Chem. Soc.* 133, 5756–5759. doi: 10.1021/ja201118f
- Lukatskaya, M. R., Feldblyum, J. I., Mackanic, D. G., Lissel, F., Michels, D. L., Cui, Y., et al. (2018). Concentrated mixed cation acetate "water-in-salt" solutions as green and low-cost high voltage electrolytes for aqueous batteries. *Energy Environ. Sci.* 11, 2876–2883. doi: 10.1039/c8ee00833g
- Manalastas, W. J., Kumar, S., Verma, V., Zhang, L. P., Yuan, D., and Srinivasan, M. (2018). Water in rechargeable multivalent-ion batteries: an electrochemical Pandora's box. *ChemSusChem* 12, 379–396. doi: 10.1002/cssc.201801523
- Marcus, Y. (2009). Effect of ions on the structure of water: structure making and breaking. *Chem. Rev.* 109, 1346–1370. doi: 10.1021/cr8003828
- McEldrew, M., Goodwin, Z. A. H., Kornyshev, A. A., and Bazant, M. Z. (2018). Theory of the double layer in water-in-salt electrolytes. *J. Phys. Chem. Lett.* 9, 5840–5846. doi: 10.1021/acs.jpcl.8b02543
- Nakamoto, K., Sakamoto, R., Ito, M., Kitajou, A., and Okada, S. (2017). Effect of concentrated electrolyte on aqueous sodium-ion battery with sodium manganese hexacyanoferrate cathode. *Electrochim. Acta* 85, 179–185. doi: 10.5796/electrochemistry.85.179
- Nakamoto, K., Sakamoto, R., Sawada, Y. K., Ito, M., and Okada, S. (2018). Over 2 V aqueous sodium-ion battery with prussian blue-type electrodes. *Small Methods* 3:1800220. doi: 10.1002/smt.201800220
- Nakayama, Y., Senda, Y., Kawasaki, H., Koshitani, N., Hosoi, S., Kudo, Y., et al. (2015). Sulfone-based electrolytes for aluminium rechargeable batteries. *Phys. Chem. Chem. Phys.* 17, 5758–5766. doi: 10.1039/c4cp02183e
- Pan, W. D., Wang, Y. F., Zhang, Y. G., Kwok, H. Y. H., Wu, M. Y., Zhao, X. L., et al. (2019). A low-cost and dendrite-free rechargeable aluminium-ion battery with superior performance. *J. Mater. Chem. A* 7, 17420–17425. doi: 10.1039/c9ta05207k
- Peng, N., Zhao, N., Zhang, Z. G., Wan, H., Lin, H., Liu, M., et al. (2017). Stabilizing Li/electrolyte interface with a transplantable protective layer based on nanoscale LiF domains. *Nano Energy* 39, 662–672. doi: 10.1016/j.nanoen.2017.07.052
- Rasul, S., Suzuki, S., Yamaguchi, S., and Miyayama, M. (2012). High capacity positive electrodes for secondary Mg-ion batteries. *Electrochim. Acta* 82, 243–249. doi: 10.1016/j.electacta.2012.03.095
- Reber, D., Kühnel, R. S., and Battaglia, C. (2019). Suppressing crystallization of water-in-salt electrolytes by asymmetric anions enables low-temperature

- peration of high-voltage aqueous batteries. *ACS Materials Lett.* 1, 44–51. doi: 10.1021/acsmaterialslett.9b00043
- Rudd, E. J., and Gibbons, D. W. (1994). High energy density aluminum/oxygen cell. *J. Power Sources* 47, 329–340. doi: 10.1016/0378-7753(94) 87012-8
- Shin, J., Choi, D. S., Lee, H. J., Jung, Y. S., and Choi, J. W. (2019). Hydrated intercalation for high-performance aqueous zinc ion batteries. *Adv. Energy Mater.* 9:1900083. doi: 10.1002/aenm.201900083
- Song, J., Noked, M., Gillette, E., Duay, J., Rubloff, G., and Lee, S. B. (2015). Activation of a MnO₂ cathode by water-stimulated Mg²⁺ insertion for a magnesium ion battery. *Phys. Chem. Chem. Phys.* 17, 5256–5264. doi: 10.1039/c4cp05591h
- Song, M., Tan, H., Chao, D. L., and Fan, H. J. (2018). Recent advances in Zn-ion batteries. *Adv. Fun. Mater.* 28:1802564. doi: 10.1002/adfm.201802564
- Su, D. W., McDonang, A., Qiao, S.-Z., and Wang, G. X. (2016). High-capacity aqueous potassium-ion batteries for large-scale energy storage. *Adv. Mater.* 29:1604007. doi: 10.1002/adma.201604007
- Sun, X. Q., Duffort, V., Mehdi, B. L., Browning, N. D., and Nazar, L. F. (2016). Investigation of the mechanism of Mg insertion in birnessite in nonaqueous and aqueous rechargeable Mg-ion batteries. *Chem. Mater.* 28, 534–542. doi: 10.1021/acs.chemmater.5b03983
- Suo, L. M., Borodin, O., Gao, T., Olguin, M., Ho, J., Fan, X. L., et al. (2015). "Water-in-salt" electrolyte enables high-voltage aqueous lithium-ion chemistries. *Science* 350, 938–943. doi: 10.1126/science.aab1595
- Suo, L. M., Borodin, O., Sun, W., Fan, X. L., Yang, C. Y., Wang, F., et al. (2016). Advanced high-voltage aqueous lithium-ion battery enabled by "water-in-bisalt" electrolyte. *Angew. Chem. Int. Ed.* 55, 7136–7141. doi: 10.1002/ange.201602397
- Suo, L. M., Borodin, O., Wang, Y. S., Rong, X. H., Sun, W., Fan, X. L., et al. (2017). "Water-in-salt" electrolyte makes aqueous sodium-ion battery safe, green, and long-lasting. *Adv. Energy Mater.* 7:1701189. doi: 10.1002/aenm.201701189
- Suo, L. M., Hu, Y. S., Li, H., Armand, M., and Chen, L. Q. (2013). A new class of solvent-in-salt electrolyte for high-energy rechargeable metallic lithium batteries. *Nat. Commun.* 4:1481. doi: 10.1038/ncomms2513
- Vatamanu, J., and Borodin, O. (2018). Ramifications of water-in-salt interfacial structure at charged electrodes for electrolyte electrochemical stability. *J. Phys. Chem. Lett.* 8, 4362–4367. doi: 10.1021/acs.jpcclett.7b01879
- Wang, F., Borodin, O., Gao, T., Fan, X. L., Sun, W., Han, F. D., et al. (2018a). Highly reversible zinc metal anode for aqueous batteries. *Nat. Mater.* 17, 543–549. doi: 10.1038/s41563-018-0063-z
- Wang, F., Fan, X. L., Gao, T., Sun, W., Ma, Z. H., Yang, C. Y., et al. (2017). High-voltage aqueous magnesium ion batteries. *ACS Cent. Sci.* 3, 1121–1128. doi: 10.1021/acscentsci.7b00361
- Wang, F. X., Yu, F., Wang, X. W., Chang, Z., Fu, L. J., Zhu, Y. S., et al. (2016). Aqueous rechargeable zinc/aluminum ion battery with good cycling performance. *ACS Appl. Mater. Interfaces* 8, 9022–9029. doi: 10.1021/acscami.5b06142
- Wang, G., Fu, L., Zhao, N., Yang, L., Wu, Y., and Wu, H. (2007). An aqueous rechargeable lithium battery with good cycling performance. *Angew. Chem. Int. Ed.* 46, 295–297. doi: 10.1002/anie.200603699
- Wang, H., Wang, M., and Tang, Y. B. (2018b). A novel zinc-ion hybrid supercapacitor for long-life and low-cost energy storage applications. *Energy Storage Mater.* 13, 1–7. doi: 10.1016/j.ensm.2017.12.022
- Wang, P. P., Chen, Z., Wang, H., Ji, Z. Y., Feng, Y. P., Wang, J. Q., et al. (2020). A high performance flexible aqueous Al ion rechargeable battery with long cycle life. *Energy Storage Mater.* 25, 426–435. doi: 10.1016/j.ensm.2019.09.038
- Wang, Y. G., Yi, J., and Xia, Y. G. (2012). Recent progress in aqueous lithium-ion batteries. *Adv. Energy Mater.* 2, 830–840. doi: 10.1002/aenm.201200065
- Wang, Y. S., Liu, J., Lee, B., Qiao, R. M., Yang, Z. Z., Xu, S. Y., et al. (2015). Ti-substituted tunnel-type Na_{0.44}MnO₂ oxide as a negative electrode for aqueous sodium-ion batteries. *Nat. Commun.* 6, 1–10. doi: 10.1038/ncomms7401
- Wessells, C. D., Peddada, S. V., Huggins, R. A., and Cui, Y. (2011). Nickel hexacyanoferrate nanoparticle electrodes for aqueous sodium and potassium ion batteries. *Nano Lett.* 11, 5421–5425. doi: 10.1021/nl203193q
- Wu, X. Y., Luo, Y., Sun, M. Y., Qian, J. F., Cao, Y. L., Ai, X. P., et al. (2015). Low-defect Prussian blue nanocubes as high capacity and long life cathodes for aqueous Na-ion batteries. *Nano Energy* 13, 117–124. doi: 10.1016/j.nanoen.2015.02.006
- Xia, L., Yu, L. P., Hu, D., and Chen, G. Z. (2017). Electrolytes for electrochemical energy storage. *Mater. Chem. Front.* 1, 584–618. doi: 10.1039/c6qm00169f
- Xie, X. S., Liang, S. Q., Gao, J. W., Guo, S., Guo, J. B., Wang, C., et al. (2020). Manipulating the ion-transfer kinetics and interface stability for high-performance zinc metal anodes. *Energy Environ. Sci.* 13, 503–510. doi: 10.1039/C9EE03545a
- Xu, C. J., Chen, Y. Y., Shi, S., Li, J., Kang, F. Y., and Su, D. S. (2015). Secondary batteries with multivalent ions for energy storage. *Sci. Rep.* 5:14120. doi: 10.1038/srep14120
- Xu, K., and Wang, C. S. (2016). Batteries: widening voltage windows. *Nat. Energy* 1:16161. doi: 10.1038/nenergy.2016.161
- Yamada, Y., Usui, K., Sodeyama, K., Ko, S., Tateyama, Y., and Yamada, A. (2016). Hydrate-melt electrolytes for high-energy-density aqueous batteries. *Nat. Energy* 1:16129. doi: 10.1038/nenergy.2016.129
- Yan, J., Wang, J., Liu, H., Bakenov, Z., Gosselink, D., and Chen, P. (2012). Rechargeable hybrid aqueous batteries. *J. Power Sources* 216, 222–226. doi: 10.1016/j.jpowsour.2012.05.063
- Yang, C., Chen, J., Ji, X., Pollard, T. P., Lu, X. J., Sun, C. J., et al. (2019a). Aqueous Li-ion battery enabled by halogen conversion–intercalation chemistry in graphite. *Nature* 569, 245–250. doi: 10.1038/s41586-019-1175-6
- Yang, H. C., Li, H. C., Li, J., Sun, Z. H., He, K., Cheng, H.-M., et al. (2019b). The rechargeable aluminum battery: opportunities and challenges. *Angew. Chem. Int. Ed. Engl.* 58, 11978–11996. doi: 10.1002/anie.201814031
- Yoo, H. D., Shterenberg, I., Gofer, Y., Gershinshy, G., Pour, N., and Aurbach, D. (2013). Mg rechargeable batteries: an on-going challenge. *Energy Environ. Sci.* 6:2265. doi: 10.1039/c3ee40871j
- Zhang, C., Holoubek, J., Wu, X. Y., Daniyar, A., Zhu, L. D., Chen, C., et al. (2018). ZnCl₂ water-in-salt electrolyte for reversible Zn metal anode. *Chem. Commun.* 54, 14097–14099. doi: 10.1039/c8cc07730d
- Zhang, J. Y., Yao, X. H., Misra, R. K., Cai, Q., and Zhao, Y. L. (2020). Progress in electrolytes for beyond-lithium-ion batteries. *J. Mater. Sci. Technol.* 44, 237–257. doi: 10.1016/j.jmst.2020.01.017
- Zhang, L. Y., Chen, L., Zhou, X. F., and Liu, Z. P. (2014). Towards high-voltage aqueous metal-ion batteries beyond 1.5 V: the Zinc/Zinc hexacyanoferrate system. *Adv. Energy Mater.* 5:1400930. doi: 10.1002/aenm.201400930
- Zhang, X. G. (1996). *Corrosion and Electrochemistry of Zinc*. Berlin: Springer, 283–303. doi: 10.1007/978-1-4757-9877-7_9
- Zhao, J. W., Li, Y. Q., Peng, X., Dong, S. M., Ma, J., Cui, G. L., et al. (2016). High-voltage Zn/LiMn_{0.8}Fe_{0.2}PO₄ aqueous rechargeable battery by virtue of "water-in-salt" electrolyte. *Electrochem. Commun.* 69, 6–10. doi: 10.1016/j.elecom.2016.05.014
- Zhao, Q., Zachman, M. J., Al Sadat, W. I., Zheng, J. X., Kourkoutis, L. F., and Archer, L. (2018). Solid electrolyte interphases for high-energy aqueous aluminum electrochemical cells. *Sci. Adv.* 4:eau8131. doi: 10.1126/sciadv.aau8131
- Zhao, X. Y., Zhao-Karger, Z. R., Fichtner, M., and Shen, X. D. (2020). Halide-Based Materials and Chemistry for Rechargeable Batteries. *Angew. Chem. Int. Ed.* 59, 5902–5949. doi: 10.1002/anie.201902842
- Zheng, Q. F., Miura, S., Miyazaki, K., Ko, S., Watanabe, E., Okoshi, M., et al. (2019). Sodium- and potassium-hydrate melts containing asymmetric imide anions for high-voltage aqueous batteries. *Angew. Chem. Int. Ed. Engl.* 58, 14202–14207. doi: 10.1002/anie.201908830
- Zhou, A. X., Jiang, L. W., Yue, J. M., Tong, Y. X., Zhang, Q. Q., Lin, Z. J., et al. (2019). Water-in-salt electrolyte promotes high capacity FeFe(CN)₆ cathode for aqueous Al-ion battery. *ACS Appl. Mater. Interfaces* 11, 41356–41362. doi: 10.1021/acscami.9b14149

Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Copyright © 2020 Wang, Meng, Sun, Liu and Hou. This is an open-access article distributed under the terms of the Creative Commons Attribution License (CC BY). The use, distribution or reproduction in other forums is permitted, provided the original author(s) and the copyright owner(s) are credited and that the original publication in this journal is cited, in accordance with accepted academic practice. No use, distribution or reproduction is permitted which does not comply with these terms.