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# High-Voltage Electrolytes for Aqueous Energy Storage Devices

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Dedicated to the 100th Anniversary of Nankai University

Aqueous energy storage devices have been considered as one of the most promising candidates for large-scale energy storage owing to their high safety and low cost. However, the narrow stability voltage window of electrolytes originating from the decomposition of water limits their energy density. In this Minireview, we discuss the limited energy density of aqueous energy storage devices in detail, and then the water decom-

position mechanism and corresponding key factors. Furthermore, we present the comprehensive overview of the strategies for increasing the stability of aqueous electrolytes, including redox-active additives, pH regulation of electrolytes, utilization of water-in-salt electrolytes, and selection of highly stable electrolyte salts. Finally, this Minireview also offers insights in the design of high-voltage aqueous electrolytes.

## 1. Introduction

The continuous consumption of fossil fuel raises the hazard of energy crises and environmental problems. Thus, it is inevitable to explore renewable energy sources, such as solar, wind, and tide.<sup>[1]</sup> However, these renewable energy sources are intermittent and unstable. One effective strategy to collect the energy is to integrate them with electrical grid. Therefore, large-scale energy storage devices are required to store the electricity, such as batteries.<sup>[2]</sup> The common energy storage devices are lithium-ion batteries based on organic electrolytes, which display high energy density, long cycle stability, and high energy efficiency.<sup>[3]</sup> But their applications on electrical grid are impeded by their low safety originating from the inherent flammability of organic electrolytes. In addition, the organic electrolytes are often toxic intrinsically and result in environmental pollutions. Furthermore, the cost is high because of the requirement of rigorous environment during cell assembly processes and the application of high cost electrode materials and electrolytes.

Compared with organic electrolytes, aqueous electrolytes exhibit various merits.<sup>[4]</sup> First, aqueous electrolytes display high safety due to the essentially non-flammable character. Second, aqueous electrolytes are often nontoxic and eco-friendly. Third, the price of the aqueous electrolytes is relatively low and the rigorous manufacturing processes in energy storage devices based on organic electrolytes are avoided. Fourth, the ionic conductivity of the aqueous electrolytes is often higher than

that of organic electrolytes by 2 orders of magnitude. Consequently, energy storage devices based on aqueous electrolytes have been considered as one of the most promising candidates for large-scale energy storage. However, aqueous electrolytes show much narrower stable voltage windows (approximately 1.23 V for pure water) than organic electrolytes due to the electrolysis of water.<sup>[5]</sup> This seriously limits the energy density of aqueous energy storage devices. Furthermore, the high hydrogen evolution potential and low oxygen evolution potential restrict the applications of low potential anodes and high potential cathodes, respectively. Only the materials whose redox potential is located between the hydrogen evolution potential and oxygen evolution potential are suitable for the aqueous energy storage devices.<sup>[6]</sup> Therefore, the energy density of aqueous energy storage devices is much lower than that of organic systems at current stage. As a result, broadening the stable voltage windows of aqueous electrolytes is crucial for the further development of aqueous energy storage systems with high energy density.

In this minireview, we will concisely describe the limited energy density of aqueous energy storage devices, discuss the electrochemical principles of water decomposition in detail, and summarize the design strategies for high-voltage aqueous electrolytes including redox-active additives, pH regulation of electrolytes, utilization of water-in-salt electrolytes, and selection of highly stable electrolyte salts (Figure 1). In the final section, we present the further developments and perspectives on designing the high-voltage electrolytes for aqueous energy storage devices.

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## 2. The Limited Energy Density of Aqueous Energy Storage Devices

The common aqueous energy storage devices are supercapacitors and batteries. The two systems are quite different on

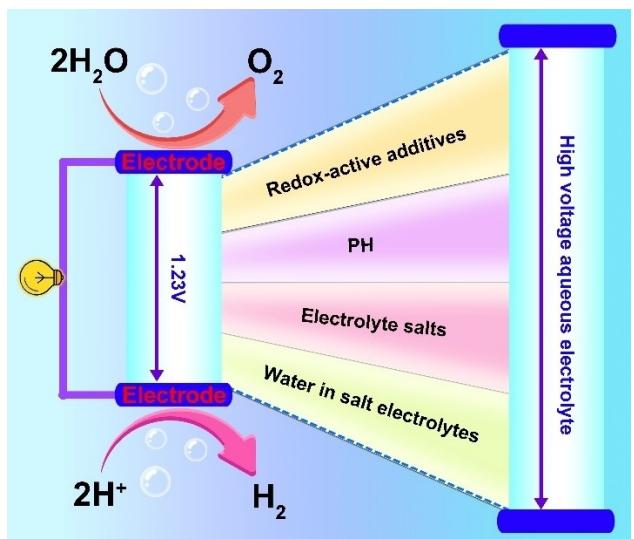


Figure 1. An overview of high-voltage aqueous electrolytes, including their decomposition mechanism and voltage improvement strategies.

the energy storage mechanism. The supercapacitors store energy by adsorbing electrolyte ions and/or fast redox reactions on the surface of electrodes, which are generally categorized into electrical double-layer capacitors and pseudocapacitors, respectively.<sup>[7]</sup> However, the batteries often implement rocking-chair mechanism, which involves the shuttle of charge carriers between cathode and anode accompanying with the redox of electrode materials.<sup>[8]</sup>

Owing to the fast ion adsorption/desorption or surface redox reactions, supercapacitors often present high output power and long cycling stability.<sup>[9]</sup> However, their energy density is relatively lower compared with batteries. According to the equation:  $E = 1/2 CV^2$  (where  $E$ ,  $C$ , and  $V$  represent the energy density, capacitance, and operating voltage, respectively), the capacitance and the operating voltage play a key impact on the energy density.<sup>[10]</sup> Many works are focused on

developing electrode materials with high capacitance.<sup>[11]</sup> However, the efforts on enhancing the operating voltage of aqueous electrolytes are relatively lacked. The operating voltage can be obtained via the equation  $V = P_C - P_A$  ( $P_C$  and  $P_A$  are the potentials of cathode and anode, respectively, which can be monitored via three-electrode systems). Therefore, increasing the  $P_C$  and decreasing the  $P_A$  could result in a high operating voltage. However, the  $P_C$  and  $P_A$  are seriously limited by the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER), respectively. As a result, aqueous electrolytes usually display a narrow thermodynamic stable potential window.

Compared with supercapacitors, aqueous batteries exhibit higher energy density. However, it cannot still catch up with that of batteries based on organic electrolytes due to limited electrochemical stable potential window.<sup>[12]</sup> In order to enhance the energy density of aqueous batteries, anode materials that have a low working potential and cathode materials that have a high working potential are preferred. However, at pH 7.0, the cathodic and anodic decomposition of water are limited at 2.62 V and 3.85 V vs. Li<sup>+</sup>/Li, respectively (taking aqueous lithium ion batteries as examples). Therefore, most promising anodes and cathodes whose working potentials beyond these limits are not applicable for aqueous lithium ion batteries, such as Li metal (0.0 V vs. Li<sup>+</sup>/Li), graphite (0.10 V vs. Li<sup>+</sup>/Li), silicon (0.30 V vs. Li<sup>+</sup>/Li), LiMnO<sub>2</sub> (4.10 V vs. Li<sup>+</sup>/Li), LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub> (4.20 V vs. Li<sup>+</sup>/Li), and LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> (4.60 V vs. Li<sup>+</sup>/Li).<sup>[6]</sup> Only those materials with working potential situated in the narrow electrochemical stable potential window of water have been mainly considered as potential electrode materials, such as VO<sub>2</sub> anode (2.70 V vs. Li<sup>+</sup>/Li) and LiFePO<sub>4</sub> cathode (3.50 V vs. Li<sup>+</sup>/Li).<sup>[11]</sup> However, the assembled aqueous batteries often exhibit low voltage below 1.5 V and energy density below 100 Wh kg<sup>-1</sup>.



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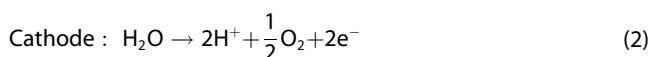
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### 3. Electrochemical Principles of Water Decomposition

The water decomposition often exists in the aqueous electrochemical energy storage systems, resulting in their irreversible electrochemical reactions. In general, the reaction of water decomposition can be formulated as follows [Eq. (1)]:<sup>[13]</sup>



In the electrochemical energy storage devices, such reaction is divided into two parts, where the OER occurs at the cathode and the HER happens at the anode. The two reactions can be chemically expressed as follows [Eqs. (2), (3)]:



The minimum thermodynamic voltage ( $E$ ) that makes the water decomposition happen can be calculated by the thermodynamic equation [Eq. (4)]:

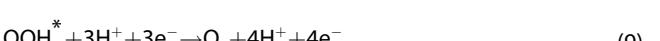
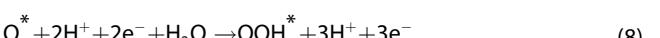
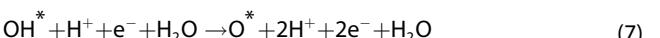
$$\Delta G = -nFE \quad (4)$$

where the  $\Delta G$  is the Gibbs free energy change of the water decomposition process,  $n$  is the transfer electron number, and  $F$  is the Faraday constant, which is equal to the  $96485 \text{ C mol}^{-1}$ , respectively. At the standard condition, where the temperature is  $25^\circ\text{C}$  and the pressure is 1 atm, an energy input of  $\Delta G = 237.1 \text{ kJ mol}^{-1}$  is required to achieve the electrochemical water decomposition and the  $E$  of the water decomposition process is calculated to be  $1.23 \text{ V}$ .<sup>[14]</sup> However, the practical applied voltage is higher than the theoretical value due to the sluggish kinetics of the HER and OER. Therefore, the excess voltage is needed, which is defined as the overpotential ( $\eta$ ), consisting of intrinsic activation barriers existing on the anode ( $\eta_a$ ) and cathode ( $\eta_b$ ), as well as the overpotential ( $\eta_{\text{other}}$ ) from the aqueous solution, the resistances, etc.<sup>[15]</sup> Therefore, the actual voltage of the water decomposition can be represented as [Eq. (5)]:

$$E = 1.23 + \eta_a + \eta_b + \eta_{\text{other}} \quad (5)$$

It is worth noting that the practical water decomposition process is complicated. Taking the HER as an example, in general, the HER involves three possible reaction routes.<sup>[16]</sup> The first one is the Volmer step:  $\text{H}^+ + \text{e}^- \rightarrow \text{H}_{\text{ads}}$ , where a proton reacts with an electron to produce the adsorbed hydrogen atom ( $\text{H}_{\text{ads}}$ ) on the electrode surface. After the production of the  $\text{H}_{\text{ads}}$ , the HER can continually proceed by Tafel step:  $2\text{H}_{\text{ads}} \rightarrow \text{H}_2$  or the Heyrovsky step:  $\text{H}_{\text{ads}} + \text{H}^+ + \text{e}^- \rightarrow \text{H}_2$  or both. It can be seen that the  $\text{H}_{\text{ads}}$  is always participated in the HER reaction. If the generated  $\text{H}_{\text{ads}}$  was attached on the electrode

surface tightly, the excess voltage should be utilized to overcome the increased hydrogen adsorption Gibbs free energy change  $\Delta G_{\text{Hads}}$  (Figure 2a). The similar oxygen adsorption Gibbs free energy change  $\Delta G_{\text{Oads}}$  phenomenon is also demonstrated in OER, and the additional voltage is also necessitated to make the OER happen. Similar to the HER reaction mechanism, the OER consists of the four-electron charge-transfer steps [Eqs. (6)–(9)]:



The OER involves three adsorbed intermediates ( $\text{OH}^*$ ,  $\text{O}^*$ , and  $\text{OOH}^*$ ), and the adsorption Gibbs free energy change of oxygen species ( $\Delta G_{\text{Oads}}$ ) is different (Figure 2b). Owing to the more complicated adsorption processes in OER, its overpotential is often high.

The overpotential values of the water decomposition depend on the pH values of the aqueous electrolytes. According to the Nernst equation, the electrode potential  $b_k$ ;  $\phi_{\text{H}+/H_2}$  can be expressed as [Eq. (10)]:

$$\varphi_{\text{H}+/H_2} = \varphi^\ominus + \frac{RT}{F} \ln(a_{\text{H}^+}) \quad (10)$$

where  $\varphi^\ominus$  is the standard potential of HER and is equaled to  $0 \text{ V}$ ;  $R$  and  $F$  is thermodynamic constant and Faraday constant, respectively;  $T$  is thermodynamic temperature;  $a_{\text{H}^+}$  is the activity concentration of proton in electrolyte, which depends on the pH of electrolyte [Eq. (11)]:

$$a_{\text{H}^+} = 10^{-\text{pH}} \quad (11)$$

It is noted that the increased pH can reduce the  $a_{\text{H}^+}$ , thus resulting in the degradation of activity of the proton. Therefore, the  $\phi_{\text{H}+/H_2}$  is more negative than the case at standard condition. Thus, a larger overpotential for HER is achieved in neutral electrolytes than in acidic electrolytes. Furthermore, according to the Nernst equation, the  $\phi_{\text{H}+/H_2}$  is temperature-dependent. It shifts positively when improving the temperature of the electrolytes. In addition, the concentration of electrolytes

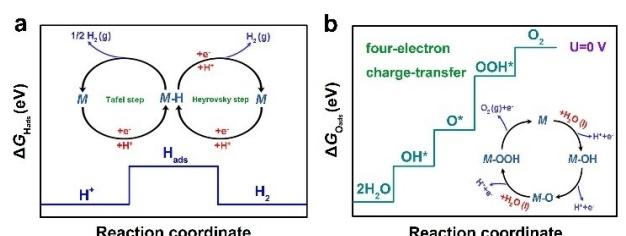


Figure 2. The Gibbs free energy change of (a) HER and (b) OER.

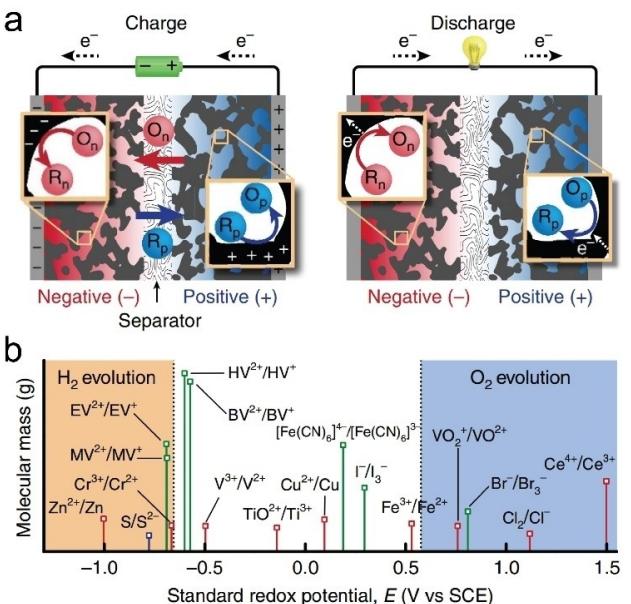
also influence the overpotential values of HER and OER.<sup>[17]</sup> Owing to the strong interaction between the solvated ions and water molecules, the electrolytes with high concentration can reduce the water activity, and thus increase the overpotential of HER and OER. Furthermore, another issue that further increases the overpotential of the water decomposition is the interface effect. The inferior surface wetting of the aqueous electrolytes will lead to the decrease of effective surface area, resulting in the increase of the interfacial resistance. Therefore, the excess voltage is needed to overcome the electrical and/or ionic resistances of the aqueous electrolytes. Therefore, by the selection of solvent ions and the optimization of the aqueous electrolytes, the overpotential of HER and OER can be rationally extended, and thus leading to the increase of voltage for the water decomposition. As a result, the electrochemical stable potential window of the aqueous electrolytes can be increased.

## 4. Design Strategies for High-voltage Electrolytes

### 4.1. Redox-Active Additives

Redox-active additives have been widely used in the aqueous electrolytes of supercapacitors. They can increase the capacitance because of the additional faradic charge/discharge process. Besides, they can also enhance the operating voltage by reasonably adjusting their species. Redox-active additives can be mainly divided into cathode additives and anode additives according to their redox potentials. Cathode additives should have a redox potential near or slightly more positive than the oxygen evolution potential. The redox potential of anode additives should be near or slightly lower than hydrogen evolution potential. During charge process, cathode additives are oxidized and the corresponding species adsorb on the surface of cathode by electrostatic or physical manner, while anode additives are reduced and then the reduced products deposit on the surface of anodes (Figure 3a). During discharge process, reverse reactions occur on the surface of electrodes. Owing to their fast reaction kinetics, the redox reactions would happen prior to the decomposition of water in electrolytes. As a result, the stable potential window of electrolytes is broadened.

A number of redox-active additives have been developed (Figure 3b), such as benzyl viologen (BV), ethyl viologen (EV), heptyl viologen (HV), methyl viologen (MV), vanadium complexes, indigo carmine, halides, copper salts, methylene blue, and quinones, and their influences on the operating voltage were also investigated.<sup>[18]</sup> For example, Chun et al. used 1 M KBr/0.1 M MVCl<sub>2</sub> (MV=methyl viologen) as the electrolytes of supercapacitor based on activated-carbon electrodes, and the supercapacitor still displayed stable electrochemical performance when the operating voltage was enlarged to 1.4 V.<sup>[19]</sup> Such high stable potential window of electrolytes is attributed to the redox-active species (Br<sup>-</sup>/Br<sub>3</sub><sup>-</sup> and MV<sup>2+</sup>/MV<sup>+</sup>). The Br<sup>-</sup>/Br<sub>3</sub><sup>-</sup> possesses a slightly higher redox potential than oxygen



**Figure 3.** (a) Schematic displaying capacitive and faradaic charge-storage processes of redox-active additives in electrolyte. (b) Reduction potentials of the redox-active additives relative to the stability window of water at neutral pH (white region). The red, green, and blue lines are the redox couples in acidic (1 M acid), neutral and basic (1 M base) conditions, respectively. SCE, standard calomel electrode. Reproduced with permission from Ref. [19]. Copyright 2015 Nature Publishing Group.

evolution reaction, and thus it is a promising redox species to suppress OER on cathode. Furthermore, MV<sup>2+</sup>/MV<sup>+</sup> is a typical anode redox species, whose redox potential is slightly lower than hydrogen evolution reaction, and thus it would restrain the hydrogen evolution reaction. As a result, the stable potential window is broadened to 1.4 V. The redox reactions of redox-active additives could often occur prior to the decomposition of water in electrolytes. Therefore, they could limit the decomposition of water, thus resulting in broad voltage window and enhanced cycling stability. However, in some cases, it is worth noting that the redox of redox-active additives would be irreversible, which leads to undesired Coulombic efficiency, low energy efficiency, high impedance, and unsatisfied cycling stability. In addition, the shuttling of redox species between cathode and anode often results in fast self-discharge.

Redox-active additives have obvious influences on the operating voltage of aqueous electrolytes. They should possess the following characteristic physicochemical properties. First, redox-active additives own high solubility. Second, the redox reactions could be highly reversible and happen on the surface of electrodes. Third, the redox products are able to adsorb on the surface of electrodes.

### 4.2. Adjustment of pH

According to the Nernst equation, the pH of the electrolytes plays an important role in adjusting the electrode potential of the HER and OER. The theoretical electrode potential of the

HER ( $\phi_{H+/H_2}$ ) and OER ( $\phi_{H_2O/O_2}$ ) can be calculated as follows [Eqs. (12), (13)]:

$$\phi_{H+/H_2} = -0.0591 \text{ pH} \quad (12)$$

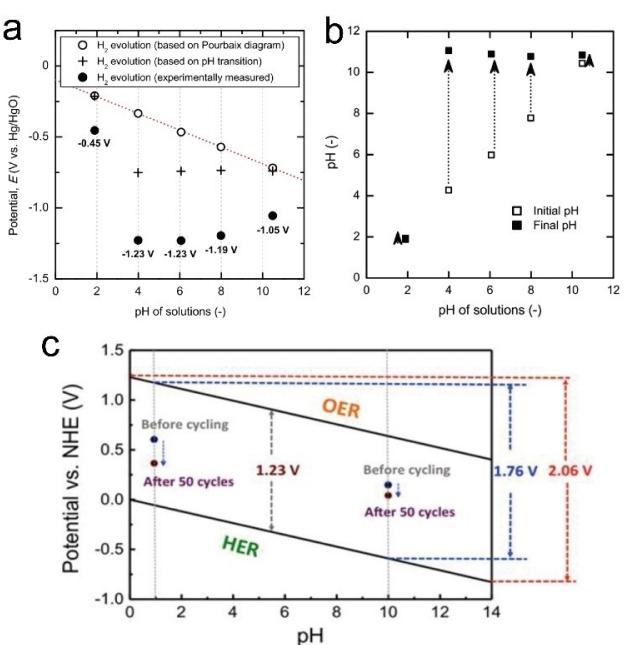
$$\phi_{H_2O/O_2} = 1.23 - 0.0591 \text{ pH} \quad (13)$$

It is noted that the electrode potentials of the HER and OER will shift negatively with the increase of the pH of the electrolytes. Therefore, by improving the pH of the electrolytes, the low potential of the HER will be achieved, broadening the voltage window of the aqueous electrolytes. Therefore, the potential of HER in the neutral electrolytes is lower than the case in acidic electrolytes. For example, the higher voltage aqueous asymmetric capacitors were achieved with neutral  $\text{Li}_2\text{SO}_4$  ( $\text{pH}=6.5$ ) than the case in acidic  $\text{BeSO}_4$  ( $\text{pH}=2.1$ ) electrolytes.<sup>[20]</sup> In the neutral  $\text{Li}_2\text{SO}_4$  electrolytes, a few  $\text{OH}^-$  species will be produced from the water reduction, and thus the local pH of the electrolytes will suddenly increase, leading to the low potential for the HER. The current oscillations attributed to the HER start at about  $-0.8 \text{ V}$  vs SHE and achieve a high HER overpotential of  $416.5 \text{ mV}$ . By in situ detecting the change of pH near the electrode/electrolyte interface during the charging process with the pH sensor, the pH value in a range of  $4\text{--}10.5$  will turn to  $11$  (Figure 4a).<sup>[21]</sup> In contrast, owing to the presence of a large amount of  $\text{H}^+$ , in the extreme acidic electrolyte, the pH is still  $2$  (Figure 4b). Therefore, the potential of the HER in such electrolyte is unchanged. According to the Nernst equation, the electrode potential of the HER in neutral

electrolytes should be located between the cases in the acidic or basic electrolytes. However, owing to the existence of a large amount of  $\text{H}^+$  or  $\text{OH}^-$  species in acidic or basic electrolytes, the variation of the pH can be neglected upon electrochemical reactions and thus the potential is similar to the initial state. In the neutral electrolytes, since the concentration of the  $\text{H}^+$  or  $\text{OH}^-$  species is too low, a sudden local pH increase during the electrochemical processes will be provoked by slight water reduction, leading to the large pH swings and thus leads to the negative shift of the electrode potential of the HER and the rapid decrease of its potential than the case in the acidic or basic electrolytes. Similarly, the increased potential for OER is also observed in the neutral electrolytes, which improves the upper limit of the voltage window of the aqueous electrolytes.<sup>[22]</sup> Therefore, one strategy that broadens the voltage windows of aqueous electrolytes can make the pH of the electrolytes to be neutral. Besides broadening the voltage windows of aqueous electrolytes, the neutral pH of electrolytes can also restrain the dissolution of electrode materials, such as vanadium-based materials and oxides, thus contributing to long term stability, high Coulombic efficiency, and slow self-discharge. In addition, by designing the dual electrolytes, the stable window of aqueous electrolytes is widened. The Nernst equation suggests that the electrode potential of HER in the alkaline solution ( $\text{pH}=14$ ) is about  $826 \text{ mV}$  and in the acidic solution ( $\text{pH}=0$ ), the electrode potential of OER is about  $1230 \text{ mV}$ , respectively.<sup>[23]</sup> Therefore, by coupling the two electrolytes together by a cation selective Nafion separator, the water decomposition voltage is up to about  $2 \text{ V}$  theoretically (Figure 4c), which is much higher than the thermodynamic limit of  $1.23 \text{ V}$ . For example, by developing the dual electrolytes with the  $0.5 \text{ M KOH}$  ( $\text{pH}=13.2$ ) electrolyte and  $1 \text{ M Na}_2\text{SO}_4$  electrolyte ( $\text{pH}=6.6$ ), the full cell based on such electrolytes is able to operate at  $1.62 \text{ V}$  without the water decomposition.<sup>[24]</sup> These smart designs of dual electrolytes will be beneficial for boosting the energy density of aqueous electrochemical energy storage devices.<sup>[25]</sup>

### 4.3. Utilization of Water-in-Salt Electrolytes

In traditional nonaqueous electrolyte systems, there is often the formation of interphase between electrolyte and electrode surfaces.<sup>[26]</sup> Such solid-electrolyte interphase is formed by sacrificial electrolyte decomposition during the initial charging process. Then, it constitutes a barrier allowing ionic conduction and forbidding electronic conduction. As a result, electrochemical stable potential window of electrolytes is expanded. Unfortunately, there is no existence of such protective interphase in relatively dilute aqueous electrolytes because the decomposition products from water, such as  $\text{H}_2$ ,  $\text{O}_2$ , or  $\text{OH}^-$ , cannot deposit on the surface of electrode. In this case, water is easy to be decomposed on the surface of electrodes. As a result, conventional aqueous batteries or supercapacitors are usually suffering from low voltage and resulting in low energy density. To solve this problem, ultra-concentrated aqueous electrolyte called "water-in-salt" electrolyte (WiSE) using lithium



**Figure 4.** (a)  $\text{H}_2$  evolution potentials based on Pourbaix diagram, experimentally measured, and pH transition at different pH value. (b) Variation of pH value during cathodic charging. Reproduced with permission from Ref. [21]. Copyright 2013 Elsevier. (c) Pourbaix diagram of water, where the potential is plotted as a function of pH values. Reproduced with permission from Ref. [23]. Copyright 2016 The Electrochemical Society.

bis(trifluoromethane sulfonyl) (LiTFSI) salt was developed.<sup>[27]</sup> Once the salt concentration increases to a certain level ( $> 5 \text{ M}$ ), the  $\text{Li}^+$  solvation sheath structure was changed as a result of insufficient water population. In particular, at  $21 \text{ M}$ , there are only 2.6 water molecules per  $\text{Li}^+$ , which can no longer effectively form solvation sheath. As a consequence, the original cation solvation sheath structure is destructed and rearranged (Figure 5a). Such crystal-like model of water-in-salt electrolyte endows TFSI<sup>-</sup> more positive reductive potential than both the isolated TFSI<sup>-</sup> and hydrogen evolution. Therefore, the TFSI<sup>-</sup> in the aqueous electrolyte is reduced prior to the HER, and then the solid-electrolyte interphase is generated at the anode-electrolyte interphase. Benefiting from the formation of the solid-electrolyte interphase, the overpotential of the HER is enlarged. As a result, the electrochemical stable potential window of electrolytes is expanded. Furthermore, the high concentration of LiTFSI in solution results in strong coordination between water molecules and  $\text{Li}^+$  ions, and thus reduces the water activity, which also suppresses HER and OER. Combined the passivation of anode and suppressed HER and OER, the potential window of such "water-in-salt" electrolyte is improved to 3 V (Figure 5b).

On the basis of WiSE, the water reactivity is further reduced when an improved WiSE is "solidified" with the formation of hydrogel (gel-WiSE) using either polyvinyl alcohol (PVA) or polyethylene oxide (PEO).<sup>[6]</sup> Besides, by introducing a second salt, the resultant ultra-high concentration ( $\sim 28 \text{ M}$ ) electrolyte containing  $21 \text{ M}$  LiTFSI and  $7 \text{ M}$  LiOTF was obtained.<sup>[28]</sup> This new class of electrolyte was defined as a "water-in-bisalt" (WiBS) electrolyte, which is effective in the formation of protective interphases on the anode along with further suppression of water activities at both anode and cathode

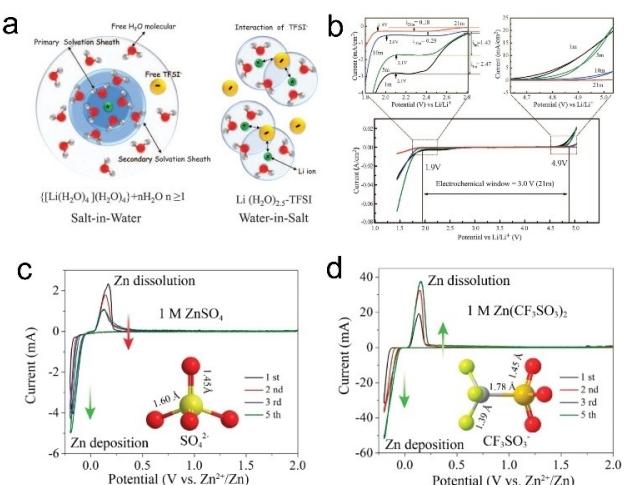
surfaces. As a result, it demonstrated a wider electrochemical stable potential window of about 3.1 V.

Beside the aqueous lithium ion batteries, this WiSE has been widely applied in other energy storage devices, such as zinc ion batteries.<sup>[29]</sup> The mixture WiSE comprising  $21 \text{ M}$  LiTFSI and  $1 \text{ M}$   $\text{Zn}(\text{CF}_3\text{SO}_3)_2$  delivers an extremely high stability in aqueous zinc-ion batteries, which OER potential is expanded to  $2.6 \text{ V}$  vs.  $\text{Zn}^{2+}/\text{Zn}$ .<sup>[30]</sup> It displays very obvious advantages compared to traditional electrolyte (such as  $1 \text{ M}$   $\text{ZnSO}_4$ ) in high-voltage battery systems. However, it is worth noting that high cost limits their practical viability. Therefore,  $30 \text{ M}$   $\text{ZnCl}_2$  WiSE may serve as another promising electrolyte for zinc-based energy storage devices.<sup>[31]</sup> By adjusting the concentration of  $5\text{--}30 \text{ M}$ , the onset potential of the HER is pushed to a lower potential and thus leads to the widened electrochemical window of the  $\text{ZnCl}_2$  electrolytes from  $1.6$  to  $2.3 \text{ V}$  vs.  $\text{Zn}^{2+}/\text{Zn}$ . In addition, water-in-salt electrolytes could effectively restrain the dissolution of electrode materials because of the decreased water activity, resulting in long term stability. However, the strong interaction between water molecules and charge carrier ions in water-in-salt electrolytes would result in low ionic conductivity and high desolvation energy during charge/discharge process, thus increasing the impedance and reducing the energy efficiency of the cells.

#### 4.4. Selection of Electrolyte Salts

Aqueous electrolytes are mainly composed of electrolyte salts and water. In addition to restraining the decomposition of water, enhancing the stability of electrolyte salts is also important for the electrochemical stable potential window of electrolytes. The cations of electrolyte salts are often  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Zn}^{2+}$ , which cannot be further oxidized and their deposition potentials except  $\text{Zn}^{2+}$  are much lower than that of HER in aqueous system. Thus, the stability of electrolyte salts is mainly determined by the anions. The common anions are classified into oxidative ( $\text{NO}_3^-$  and  $\text{ClO}_4^-$ ), reductive ( $\text{Cl}^-$  and  $\text{F}^-$ ), steady ( $\text{SO}_4^{2-}$ ), and organic ( $\text{CH}_3\text{COO}^-$ ,  $\text{CF}_3\text{SO}_3^-$ , and  $\text{N}(\text{CF}_3\text{SO}_2)_2^-$ ) anions.<sup>[32]</sup>

Among these anions,  $\text{NO}_3^-$  is a strong oxidant and could attack the electrodes. For example, in aqueous  $\text{Zn}/\text{CuHCF}$  battery system using  $\text{Zn}(\text{NO}_3)_2$  electrolytes, there is serious corrosion of the Zn anode and CuHCF cathode originating from  $\text{NO}_3^-$ .<sup>[33]</sup> Different from  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$  cannot be easily reduced although the valence of Cl in it is +7, since four O atoms are tetrahedrally coordinated with central Cl atom, resulting in a high stability. However,  $\text{ClO}_4^-$ -based aqueous electrolytes often show a high overpotential and potential safety hazard especially at high temperature. The reductive anion, such as  $\text{Cl}^-$ , is easily oxidized before the occurrence of OER of water.<sup>[34]</sup> As a result, the stable potential window of electrolytes is limited by the reductive anions instead of water.  $\text{SO}_4^{2-}$  anion possesses an extremely stable structure since it shows a regular tetrahedron structure where four S–O bonds show a similar chemical property. Thus, the  $\text{SO}_4^{2-}$  anion is widely used in aqueous energy storage devices, such as  $\text{Li}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$ , and



**Figure 5.** (a) Illustration of the evolution of the  $\text{Li}^+$  solvation sheath in diluted and water-in-salt solutions. (b) Electrochemical stability window of water-in-salt electrolyte. Reproduced with permission from Ref. [27]. Copyright 2015 American Association for the Advancement of Science. Cyclic voltammograms of Zn electrode in aqueous electrolyte of (c)  $1 \text{ M}$   $\text{ZnSO}_4$  and (d)  $1 \text{ M}$   $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ . Reproduced with permission from Ref. [34b]. Copyright 2016 American Chemical Society.

ZnSO<sub>4</sub> in supercapacitors, aqueous Li/Na ion batteries, and aqueous Zn ion batteries.<sup>[35]</sup> However, the usage of ZnSO<sub>4</sub> electrolyte in aqueous Zn ion batteries is always accompanied by the formation of basic zinc sulfates (Zn<sub>4</sub>(OH)<sub>6</sub>SO<sub>4</sub>·nH<sub>2</sub>O),<sup>[36]</sup> which would limit the electrochemical performance. Furthermore, the formation of Zn<sub>4</sub>(OH)<sub>6</sub>SO<sub>4</sub>·nH<sub>2</sub>O consumes the OH<sup>-</sup> from water and thus resulting in the production of H<sup>+</sup>,<sup>[37]</sup> which would corrupt the electrodes. Organic anions often display high stability, such as CH<sub>3</sub>COO<sup>-</sup>, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, and N(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>. Compared with inorganic anions, organic anions often possess large volume. This reduces the coordination number of H<sub>2</sub>O molecules surrounding cations and thus decreases the solvation effect of cations, especially multivalent cations such as Zn<sup>2+</sup> and Al<sup>3+</sup>.<sup>[34]</sup> As a result, electrolytes based on organic anions often exhibit fast cation migration (Figure 5c and d) and are widely used in aqueous batteries.<sup>[38]</sup> However, CH<sub>3</sub>COO<sup>-</sup> anion based electrolytes are weak alkaline owing to the hydrolysis of CH<sub>3</sub>COO<sup>-</sup> anion. It would influence the stability of electrolytes. In addition, the large organic anions are not applicable in supercapacitors, since they exhibit slower anion migration than inorganic anions. Therefore, the electrolyte salts widely used in supercapacitors are based on inorganic anions (such as SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup>) instead of organic anions.<sup>[35c]</sup>

As discussed above, highly stable electrolyte salts can not only lead to the stability of electrolytes, but also avoid the electrodes to be attacked from electrolyte salts and thus decrease the formation of byproducts, resulting in desired Coulombic efficiency, high energy efficiency, and long term stability. To achieve high stability of electrolytes, electrolyte salts could follow the following principles: (i) the redox potentials of electrolyte anions could beyond the electrolysis potential of water, (ii) electrolyte anions could possess good compatibility with electrodes, (iii) the reaction between electrolyte salts and water should be forbidden, and (iv) fast ion migration is needed.

## 5. Summary and Outlook

Aqueous energy storage devices are promising candidates for large-scale energy storage owing to their high safety and low cost. However, their energy density is strictly limited by the stability of aqueous electrolytes because the pure water displays a narrower stable voltage window of approximately 1.23 V originating from the HER and OER of water. The common aqueous energy storage devices are supercapacitors and batteries. The operating voltage plays a key impact on the energy density of supercapacitors. The operating voltage can be obtained via the equation  $V = P_C - P_A$ . However, the  $P_C$  and  $P_A$  are seriously limited by OER and HER of aqueous electrolyte. While for the aqueous batteries, most promising anodes and cathodes whose working potentials beyond the HER and OER, respectively, are not appropriate for acting as the electrodes. Actually, the stable potential window of water is higher than 1.23 V due to the activation barriers existing on the anode and cathode as well as the overpotential. Therefore, by reasonably adjusting the barriers and overpotential, the stable potential

window of electrolyte would be broadened. Various strategies are summarized, such as redox-active additives, pH regulation of electrolytes, water-in-salt electrolytes, and highly stable electrolyte salts. Owing to their fast reaction kinetics, the redox reactions would occur prior to the decomposition of water in electrolytes. As a result, the stable potential window of electrolytes is broadened. According to the Nernst equation, the pH of the electrolytes plays an important role in adjusting the electrode potential of the HER and OER. Thus, reasonable design of the pH of electrolytes can also expand the stable voltage window of aqueous electrolytes. In addition, water-in-salt electrolytes can not only decrease the activity of water, but also construct solid-electrolyte interphase between electrode and electrolyte, thus endowing the electrolyte wide voltage windows up to 3.0 V. Besides, the selecting electrolyte salts with high stability is also vital for the stability of electrolytes.

In addition to achieve broad electrochemical window of aqueous electrolytes, the above four strategies also have obvious effects on other electrochemical behaviors. In the high-voltage electrolytes with redox-active additives, the redox of redox-active additives could provide additional capacity. Moreover, redox-active additives would avoid the decomposition of water because the redox reactions of them would usually occur prior to the decomposition of water in electrolytes, thus enhancing the cycling stability. However, in some cases, such redox reactions would be irreversible, which results in undesired Coulombic efficiency, low energy efficiency, high impedance, and unsatisfied cycling stability. In addition, the shuttling of redox species between cathode and anode often leads to fast self-discharge. The water-in-salt and neutral electrolytes could restrain the dissolution of electrode materials, thus contributing to long term stability, high Coulombic efficiency, and slow self-discharge. Although water-in-salt electrolytes could provide wider voltage window than neutral electrolytes due to the inhibited water activity, the strong interaction between water molecules and charge carrier ions in water-in-salt electrolytes would result in low ionic conductivity and high desolvation energy during charge/discharge process, thus increasing the impedance and reducing the energy efficiency. In addition, the selection of highly stable electrolyte salts can not only result in the stability of electrolytes, but also avoid the electrodes to be attacked from electrolyte salts and thus decrease the formation of byproducts. However, this strategy has finite influence on restraining the decomposition of water. Therefore, reasonable selection of these strategies to broaden the electrochemical window of electrolyte is significant to achieve high performance aqueous energy storage devices.

It is noted that the reported strategies for improving the stable voltage window of aqueous electrolytes is mainly concentrated on increasing the overpotential of HER, while these strategies are not highly effective for the enhancement of the overpotential of OER. Therefore, if some strategies, such as constructing cathode-electrolyte interphase and manipulating the reaction path of OER, can be developed to increase the overpotential of OER, the stable voltage window of aqueous electrolytes would be further broadened.

Decreasing the activity of water is an effective method to broaden the stable voltage window of aqueous electrolytes. Therefore, if there is few free water in aqueous electrolytes and meanwhile the ions can still transport, the stable voltage window would be further expanded. For instance, freezing the aqueous electrolytes makes the water to be crystallized or directly using hydrous salts as electrolytes. However, the ions in such electrolytes are hard to transport. Thus, if some strategies can solve this problem, the stable voltage window of aqueous electrolytes would be boosted.

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