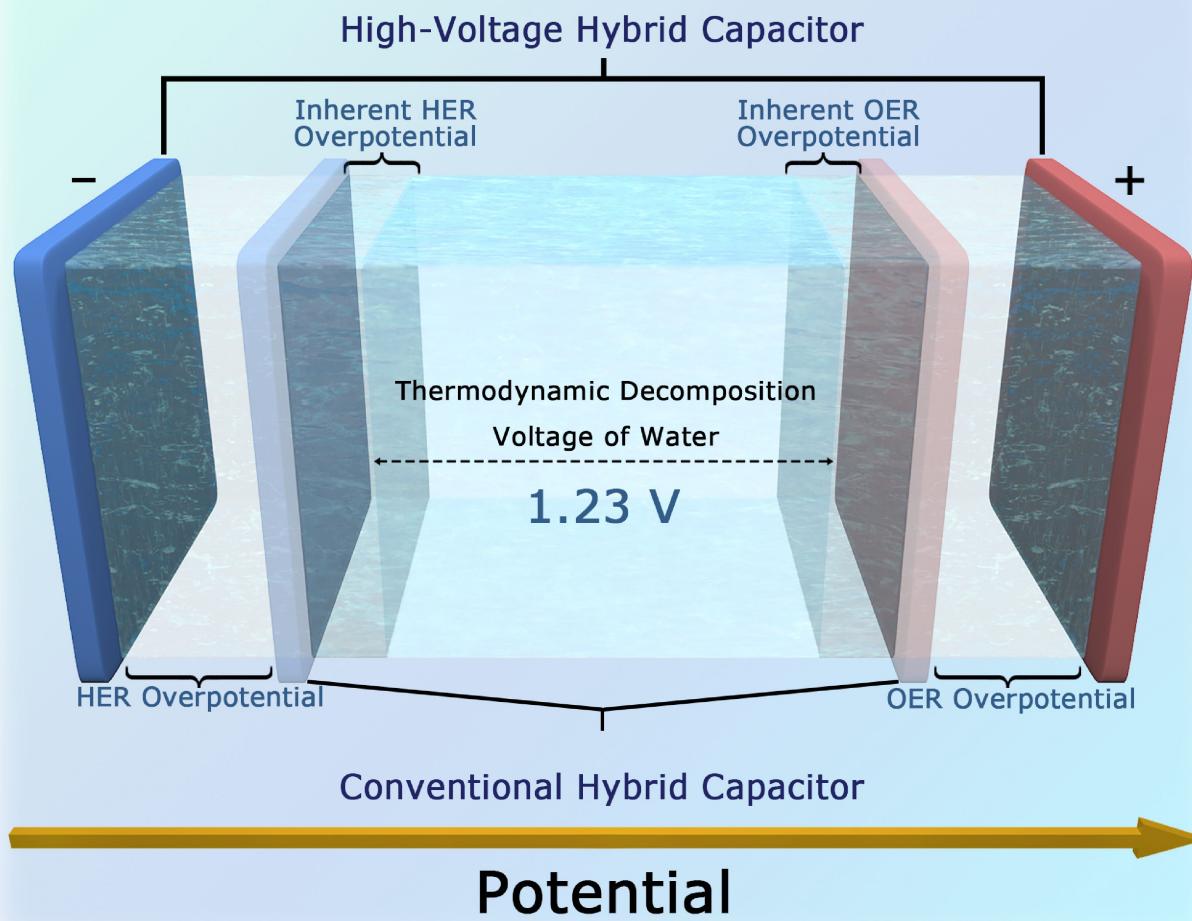


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Progress in the Regulation of Electrode/Electrolyte Interfacial Reactions toward High-voltage Aqueous Hybrid Capacitors

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Aqueous energy storage devices have drawn an increasing attention benefiting from their improved safety and reduced cost against the conventional organic systems. Hybrid capacitors that combine the advantages of both secondary batteries and electric double-layer capacitors are considered to be a promising next-generation electrical energy storage device. However, the nature of water decomposition at relatively low potential (usually ~1.23 V) limits the voltage window of aqueous hybrid capacitors and thereby hinders their applica-

tion. For this reason, it is vital to develop the aqueous hybrid capacitors that can operate in larger voltage window by means of the electrode and electrolyte engineering. This review summarizes the design of both electrodes and electrolytes, as well as the regulating strategies at their interfaces, to expand voltage window of aqueous hybrid capacitors. Furthermore, suggestions and future vision of the high-voltage aqueous hybrid capacitors are provided to pave the way for their practical application.

1. Introduction

With the rapid development of new energy resources and the exhausted fossil energy, electrochemical energy-storage technologies with high energy/power density, good safety, and long lifespan are urgently needed.^[1] However, as the most widely used electrochemical energy-storage devices, secondary batteries and electrochemical capacitors are difficult to achieve

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the above requirements simultaneously.^[2] Secondary batteries store charges by the bulk-faradic-redox reactions on electrode materials and can deliver high energy density. Nevertheless, the reactions often have sluggish kinetics. The electrode materials suffer large volume change during the reaction, which makes secondary batteries rather hard to offer high power and long lifespan.^[3] On the contrary, electrochemical capacitors store charges by means of the surface reactions on electrode materials, e.g., electric double-layer (EDL) or pseudocapacitive reaction, which enables higher power and greater cycling stability than that of secondary batteries. However, this surface charge-storage process leads to lower energy density.^[4] For EDL, it is only physical energy storage, in which ions adsorb on electrode surface by the Coulomb force.^[5] While the pseudocapacitive-type reaction is also essentially faradic-redox one and can offer higher capacitance than EDL, but it only occurs to the surface or near-surface of electrodes.^[6] In recent years, hybrid capacitors have been proposed to bridge the secondary batteries and electrochemical capacitors.^[7] Hybrid capacitors are usually formed by two electrodes with different energy storage mechanisms (EDL capacitance, pseudocapacitance or battery).^[8] Different electrodes usually have different catalytic abilities for the oxidation and reduction of water. Therefore, the hybrid capacitors with two different electrodes (*i.e.* asymmetric design) that allow a higher operating voltage than EDL capacitors are therefore selected.^[9] Combining the performance of the two electrodes, hybrid capacitors can provide higher energy density than electrochemical capacitors and meanwhile a higher power density than secondary batteries.^[10] These cells are considered as promising electrical energy storage device.^[11] The development of high-performance hybrid capacitors is expected to combine the advantages of different energy storage mechanisms to achieve ideal energy storage devices with high energy density, high power density and long lifespan.

According to the type of electrolytes, hybrid capacitors can be divided into organic and aqueous. Organic hybrid capacitors usually have wide electrochemical window.^[12] The decomposition product of organic electrolyte in the negative electrode is usually solid electrolyte interface (SEI) that conducts ions but does not conduct electrons, thereby further inhibiting electrolyte electrolysis and expanding electrochemical window to above 4 V.^[13] However, organic electrolytes have the disadvantages of high viscosity, inflammability and are much more expensive. The application of organic solvents can also lead to

harsh preparation processes and environmental unfriendliness for organic hybrid capacitors.^[14] In contrast, the electrolytes of aqueous hybrid capacitors have high ionic conductivity, low viscosity and non-flammability.^[15] The preparation of aqueous hybrid capacitors only require comparably moderate environment. All these aforementioned advantages enable the aqueous electrolytes to be suitable replacement to organic electrolytes. Unfortunately, the thermodynamic stability window of water is only 1.23 V, which makes it difficult to assemble high-voltage aqueous hybrid capacitors.^[16] The electrochemical window of commonly used acidic or alkaline electrolytes is only about 1 V.^[17] Although the neutral electrolyte can reach the

electrochemical window of 2.2 V, it has been regarded as only the result of kinetic overpotential.^[18] Therefore, the development of high-voltage aqueous hybrid capacitors is very attractive, and it is also research hotspot in the field of aqueous hybrid capacitors. Expanding the electrochemical window of aqueous electrolyte can effectively increase the operating voltage and energy density, which has profound significance of the development and application of aqueous hybrid capacitors.

Recently, researchers have done lots of work for the development of high-voltage aqueous hybrid capacitors. In order to expand electrochemical window, the key is the regulation of electrode/electrolyte interfacial reactions. The



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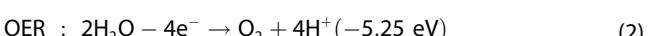
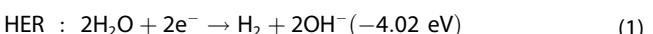
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electrochemical window can be expanded by regulating electrode and electrolyte as well as changing the interfacial reactions to inhibit the electrolysis process of water. Therefore, we summarized the structural adjustment strategies of different electrodes from the perspective of electrodes and the design strategies of different electrolyte systems from the perspective of electrolytes. We also put forward our perspective on the current situation and future development of high-voltage aqueous hybrid capacitors to provide direction and guidance for future research and application.

2. Origin of Aqueous Electrolyte Electrochemical Window

Different from the organic reagents with complex molecular structures, water molecules contain only O–H bonds. The difference in electronegativity between O and H causes H to be unable to effectively confine its only extranuclear electron, which leads the formed O–H bonds to exhibit higher ionicity and reactivity. In addition, the hydrogen bonds formed between water molecules will further weaken O–H bonds. For example, the formation of hydrogen bonds will reduce the chemical shielding of H atoms in nuclear magnetic resonance (NMR) spectroscopy, and the O–H bond stretching vibration peaks of water in Fourier transform infrared (FT-IR) spectroscopy will also be red-shifted.^[20] This means that the shared electron pair of O–H bonds further shifts to the O, which results in the ionicity of the O–H bond to increase and the bond strength to weaken. These characteristics result in stronger reactivity of water, that is, higher reduction potential and lower oxidation potential (Table 1).

However, the reactivity of water molecules does not only depend on the energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). From the electronic structure perspective, liquid water is an oxide with band gap between 8.7 eV and 8.9 eV.^[21] Actually, the electrochemical window of water is only 1.23 V limited by the hydrogen evolution reaction (HER) at negative electrode and oxygen evolution reaction (OER) at positive electrode ($\text{pH} = 7$) [Eqs. (1) and (2)].^[19c]



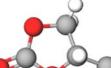
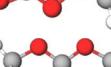
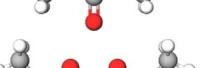
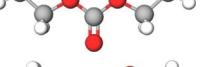
Since the water can spontaneously ionize into H^+ and OH^- , potentials for HER and OER to occur greatly depend on the acidity and alkalinity (i.e. pH) of aqueous electrolytes. Specifically, the spontaneous ionization process of water is as follows [Eq. (3)]:



The corresponding ion product constant (molar concentration product of H^+ and OH^-) is fixed value at certain temperature, which determines that the respective potentials of HER and OER have the same change when pH changes. The actual species involved in HER and OER also depend on the acidity and alkalinity of water. Figure 1 summarizes the Pourbaix diagram of water and the HER and OER processes corresponding to different pH values.^[22]

From thermodynamic viewpoint, the electrochemical window of aqueous electrolytes is stable; however, the actual HER and OER potentials are affected by kinetics. For example, neutral electrolytes can break this limitation because of the low

Table 1. Comparison of the molecular structure, oxidation potential (E_{oxd}), reduction potential (E_{red}), viscosity (η), and dielectric constant (ϵ) of water and commercial electrolyte solvents.^[19]

| Solvent | Molecular Structure ^[a] | E_{oxd} [V] (vs. SHE) ^[b] | E_{red} [V] (vs. SHE) ^[b] | H [Cp] (25 °C) | ϵ (25 °C) |
|------------------------------|---|---|---|------------------|--------------------|
| Water |  | 0.81 (pH=7) | -0.42 (pH=7) | 0.89 | 78.304 |
| Ethylene carbonate (EC) |  | 2.54 | -1.58 | 1.9 (40 °C) | 89.78 |
| Propylene carbonate (PC) |  | 2.57 | -1.8 | 2.53 | 64.92 |
| Dimethyl carbonate (DMC) |  | 2.58 | -2.18 | 0.59 (20 °C) | 3.107 |
| Diethyl carbonate (DEC) |  | 2.42 | -1.71 | 0.75 | 2.805 |
| Ethyl methyl carbonate (EMC) |  | 2.51 | | 0.65 | 2.958 |

[a] Grey balls: C; red balls: O; white balls: H. [b] SHE: Standard hydrogen electrode

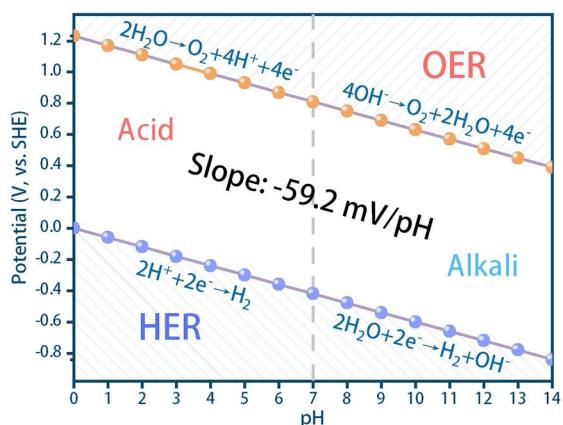


Figure 1. Pourbaix diagram and reaction processes of water showing the pH dependence of HER and OER.

concentrations of H^+ and OH^- in neutral electrolytes. When the electrolysis occurs on electrode surface, slight water decomposition will cause local H^+ or OH^- concentrations to change by orders of magnitude (such as the change of local pH from 4 to 11 in Li_2SO_4 electrolyte).^[14,23] The difference in pH between positive and negative electrodes surfaces leads to expansion of electrochemical window.^[18a] However, the wide electrochemical window obtained by adjusting pH is considered to be the result of unstable kinetic overpotential.^[18b] Therefore, other influencing factors need to be considered.

In fact, main strategy to expand electrochemical window of aqueous electrolytes is to separately regulate the reactions at two electrode/electrolyte interfaces. To this end, chemical structure of electrode surface will affect its adsorption of HER or OER reactants, and thereby influence the speed and actual potential of HER and OER from kinetic viewpoint.^[24] For example, in the same electrolyte system, MnO_2 , V_2O_5 , TiO_2 , Fe_3O_4 and other electrode materials usually have different HER and OER potentials.^[10a] Through an asymmetric design, matching the negative electrode with low HER potential and the positive electrode with high OER potential can effectively increase the overall operating voltage, which is also one of the most important advantage of hybrid capacitors. In addition to the influence of electrode on the adsorption of reactants, the redox reaction near the HER or OER potential also affects electrochemical window. The rapid redox reaction can compete with HER or OER reaction and suppress it. Another important factor is the concentrations of reactants at electrode/electrolyte interface. Reducing the concentrations of reactants at electrode interface by regulating the components of electrolyte can also suppress HER and OER. Furthermore, when water-stable SEI can be formed at the electrode/electrolyte interface, the HER or OER reactions can be suppressed more thoroughly.

In general, the electrochemical window expansion strategy of aqueous electrolytes should be accurate to each electrode/electrolyte interface. This means that the two interfacial reactions need to be designed separately to suppress the HER and OER reactions simultaneously, which is expected to overcome the narrow electrochemical window of aqueous electro-

lyte. Based on the above analysis, the specific regulation strategies for expanding electrochemical window and corresponding mechanisms were introduced separately into the two perspectives of electrodes and electrolytes.

3. Regulation Strategies for Electrode

3.1. Regulation of EDL Capacitive Electrode

The regulation of electrode is an effective strategy that is usually used to adjust the interfacial electrochemical reactions and expand electrochemical window. Since different types of electrodes have great differences in energy storage mechanisms and electrochemical behavior, most strategies are only effective for one or several types of electrodes. Therefore, the following will discuss the regulation strategies for electrodes from three perspectives: regulation of EDL capacitive electrode, pseudocapacitive electrode and battery-type electrode (Figure 2).

The characteristic of EDL capacitive electrodes is that the charge storage process does not involve redox reaction, but is only physical adsorption/desorption process. The exhibited capacitance mainly depends on the surface area and pore structures of electrode material. Therefore, carbon materials, such as activated carbon (AC) and graphene with large surface area and rich pore structures are usually used for EDL capacitive electrodes.^[25] However, for regulating electrode to expand electrochemical window, large surface area is disadvantage. As large surface area usually means large electrochemical surface area, at the same potential where electrolyte electrolysis occurs, reactions on the surface of EDL capacitive electrodes will be more intense, which is not conducive to the expansion of electrochemical window.

For EDL capacitive electrodes, an effective strategy is to reduce the catalytic activity of electrode. The overpotential of HER largely depends on the inherent electronic and electrochemical properties of electrode surface. For the HER process of water, the specific reaction mechanism is considered as follows:^[26]

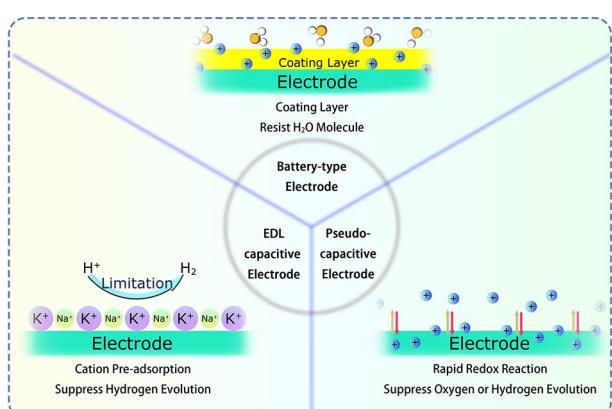
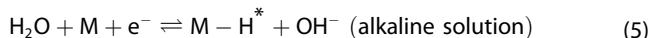
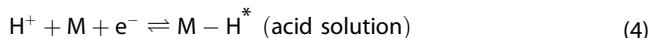
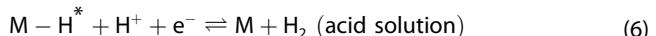


Figure 2. The mechanism of different electrode regulation strategies to expand the electrochemical window.

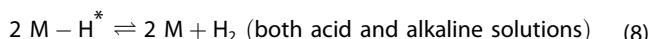
Electrochemical hydrogen adsorption (Volmer reaction) [Eqs. (4), (5)]:



Electrochemical desorption (Heyrovsky reaction) [Eqs. (6), (7)]:



or Chemical desorption (Tafel reaction) [Eq. (8)]:



In each step, the adsorption and desorption of H atoms are especially critical, where the electrode plays an important role in these processes. HER overpotential of water varies through reasonable electrode surface design and modification. The designed electrode material should have minimal catalytic activity. In other words, the weak bond in between surface and adsorbed H atom should be formed to inhibit proton-electron transfer process and the formed bond should not be easily broken to release hydrogen.^[26] For inhibiting HER, the currently reported effective method is to allow EDL capacitive electrodes to pre-adsorb cations in electrolyte through doping or electrochemical treatment.^[27] For example, the co-desorption of H⁺ (Figure 3a), Na⁺ (Figure 3b) and K⁺ (Figure 3c) on N, P, and O triple-doped graphene were simulated. The Na⁺ and K⁺ adsorption structures with the smallest chemical adsorption energy were used to adsorb protons (Figure 3d).^[27d] It was found that hydrogen adsorption energy increased from 0.07 eV to 0.13 eV for Na⁺ pre-adsorption, while for K⁺ pre-adsorption,

hydrogen adsorption energy increased from 0.07 eV to 0.16 eV (Figure 3e). The results showed that pre-adsorbed K⁺ or Na⁺ can change hydrogen adsorption energy barrier, which thereby effectively suppresses the HER reaction and expanding electrochemical window.

3.2. Regulation of Pseudocapacitive Electrode

Pseudocapacitive electrodes store charge through fast and reversible faradic redox reactions on or near the surface. Within certain potential range, the number of charges transferred by reactions also changes continuously with potential, and there is also no charge and discharge potential platform. Compared with EDL capacitive electrodes, pseudocapacitive electrodes have similar electrochemical behavior, high-power density, and the kinetics are not limited by diffusion either. Various materials have been used for pseudocapacitive electrodes, such as transition metal oxides and conductive polymers.^[28]

A mainstream and efficient strategy to regulate pseudocapacitive electrodes is to activate additional faradic redox reactions by cation pre-intercalation or oxygen defect modulation.^[29] The additional reaction needs to meet two factors: (1) its redox potential is close to the electrolysis potential of water and (2) it has faster reaction kinetics than HER or OER. In this respect, when the original electrolysis potential of electrolytes reaches, the introduced reaction can suppress HER or OER of water and thereby expand electrochemical window. For example, K⁺ was pre-intercalated during the synthesis of α -MnO₂.^[27b] In addition to the charge stored by Mn³⁺/Mn⁴⁺, the rapid insertion/extraction of Na⁺ and K⁺ was introduced during the charging and discharging process, which expanded OER of water from 1 V to 1.2 V (vs. Ag/AgCl). By combining with the cation pre-adsorption strategy of EDL capacitor electrode, 2.4 V hybrid capacitor was assembled (Figure 4). Hereafter, Na_{0.5}MnO₂ with high Na content converted from Mn₃O₄ was further designed by electrochemical oxidation.^[30] Based on the high content of Na⁺ insertion/extraction, OER potential is further expanded to 1.3 V (vs. Ag/AgCl). In addition, oxygen defect modulated Ti₂Nb₁₀O_{29-x}^[29] Na_{0.25}MnO₂,^[27c] Cr-doped δ -MnO₂, LiNi_{0.5}Mn_{1.5}O₄ converted from Ni–Mn–O nanoprism arrays,^[31] and K⁺-intercalated polyanionic molybdenophosphate^[32] have all been proven to expand electrochemical window.

Besides activating additional redox reactions, it is also reported that in recent years, the HER and OER reactions on pseudocapacitive electrodes are inhibited by structural regulation.^[33] For example, the surface-hydroxylated Mo₅O₈ can extend the electrochemical window to 2.5 V in aqueous Na⁺ system (Figure 5a–c).^[33a] Calculations confirm that in addition to the activation energy of the rate-determining step is substantially higher for OER, hydroxylated Mo₅O₈ obviously has higher activation energy than pure Mo₅O₈ for HER (Figure 5d–f). Therefore, the HER and OER reactions of the hydroxylated Mo₅O₈ in aqueous electrolytes are greatly suppressed.

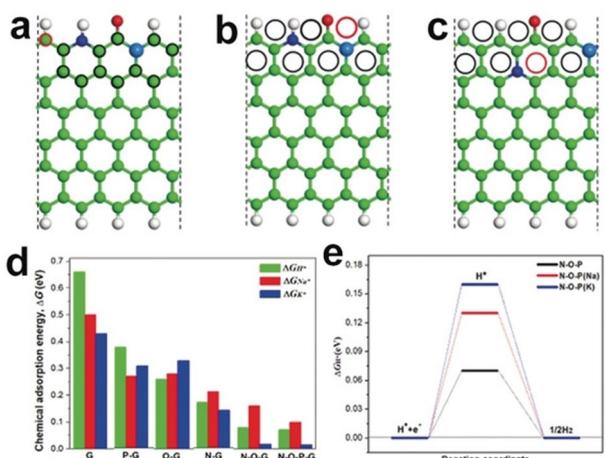


Figure 3. The N, O, and P tri-doped graphene structures used to adsorb a) H⁺ b) Na⁺, and c) K⁺. d) Minimum chemical adsorption energy on different doped graphene model for H, Na, and K adsorption. e) The three-state free energy diagram for tri-doped graphene models adsorbing Na and K and pure tri-doped graphene models. Reproduced from Ref. [27d] with permission. Copyright 2020, Wiley-VCH.

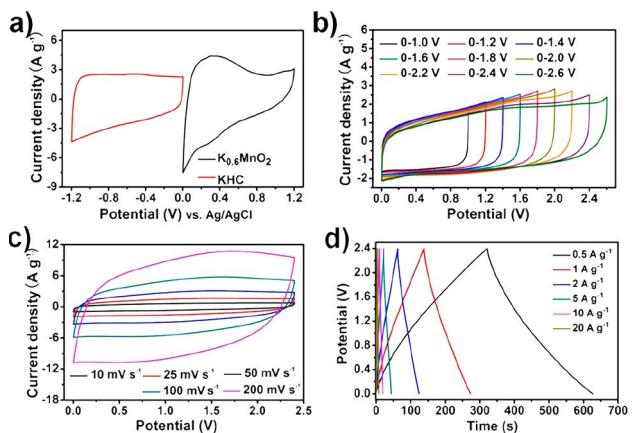


Figure 4. a) CV curves of the $K_{0.6}MnO_2$ and the K^+ -adsorbed holey carbon (KHC), b) CV of the $K_{0.6}MnO_2 \parallel$ KHC conducted at scan rate of 25 mV s^{-1} from 0 to 1 V with 0.2 V step increment to investigate the operating window, c) CV curves of $K_{0.6}MnO_2 \parallel$ KHC with potential window of 0–2.4 V, d) Galvanostatic charge/discharge profiles of $K_{0.6}MnO_2 \parallel$ KHC at various current densities. Reproduced from Ref. [27b] with permission. Copyright 2018, American Chemical Society.

3.3. Regulation of Battery-Type Electrode

Battery-type electrodes mainly rely on reversible redox reactions and ion insertion/extraction to store energy. According to the different mechanisms, battery-type electrodes can be divided into intercalation-type, conversion-type, and alloying-type electrodes. Comparing with pseudocapacitive electrodes that undergo redox reactions, battery-type electrodes react more thoroughly and exhibit higher energy density. But the reaction process is limited by sluggish ion diffusion, which affects the rate performance and power density of battery-type electrodes. Because of the limitation of energy storage mechanism, there are few reports on suppressing the HER or

OER through rapid redox reaction near water electrolysis potential. In fact, expanding the electrochemical window of aqueous battery-type electrodes is mainly achieved through coating strategy.

Coating strategy usually introduces coating layer at the electrode/electrolyte interface to change the behavior of reaction. In majority of the cases, the coating layer of battery-type electrodes is similar to SEI generated at negative electrode in organic electrolytes. And the difference is that this coating layer is not produced electrochemically *in situ* but prepared on electrode surface. Same as SEI, the artificial coating layer only conducts ions and prevents the entry of solvent molecules, but not conducts electrons. In aqueous electrolytes, hydrated metal ions desolvate water molecules on the surface of coating layer and enter the coating layer to be embedded in electrode. Water molecules cannot undergo electron transfer and electrolysis, which effectively expand electrochemical window. The coating strategy is often used on the metal anode with high theoretical capacity and the most negative potential due to its better stability. For example, Al metal negative electrode is rather difficult to be used in aqueous electrolytes due to its surface oxide layer and low standard electrode potential of -1.676 V (vs. SHE).^[34] But it has been found that the pretreatment of Al metal electrode with ionic liquid can obtain good SEI to replace the original natural surface oxide layer.^[34b] This artificial coating effectively prevents the HER of water, which can facilitate the reversible stripping and plating processes at Al metal electrode. The coating strategy can be applied to Li metal anodes that react violently with water.^[35] For instance, the gel polymer electrolyte was prepared as the first coating layer of Li metal negative electrode, and lithium ion conductor (LISICON) film was used as the second coating layer (Figure 6a).^[36] The coated Li metal negative electrode shows excellent stability in aqueous electrolytes, which is equivalent to reducing the HER potential of water to -3.04 V (vs. SHE)

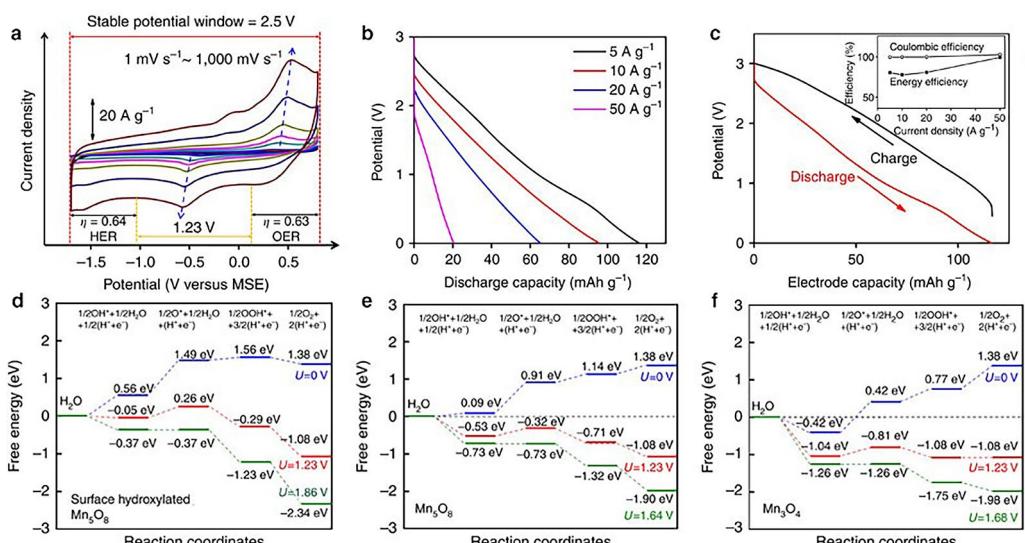


Figure 5. a) CVs show stable potential window of 2.5 V and large overpotential towards HER and OER. b–c) Charge and discharge curves of Mn_3O_4 electrode. The free energy evolution for water splitting steps at different potentials on surfaces of d) surface hydroxylated Mn_5O_8 , e) pure Mn_3O_4 and f) Mn_3O_4 predicted from density functional theory (DFT) calculations. Reproduced from Ref. [33a] with permission. Copyright 2016, Springer Nature.

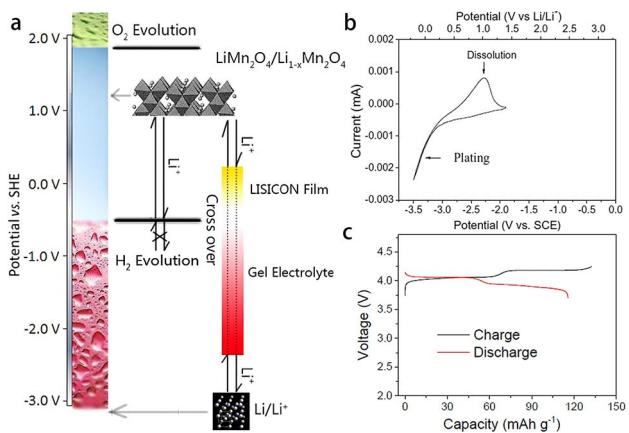


Figure 6. a) Schematic illustration of the potential of Li^+ during the movement between LiMn_2O_4 in the aqueous electrolyte and the coated lithium metal. b) CV curve in the first scan of the coated lithium metal at the scan rate of 0.1 mVs^{-1} . c) Electrochemical performance of the designed aqueous rechargeable lithium battery at the current density of 100 mA g^{-1} . Reproduced from Ref. [36] with permission. Copyright 2013, Springer Nature.

(Figure 6b–c). The Li metal or graphite was pre-coated with thin layer of 1,1,2,2-tetrafluoroethyl-2',2',2'-trifluoroethyl ether (HFE) and lithium bis(trifluoromethane) sulfonimide (LiTFSI).^[37] HFE can form unique composite interphase consisting of both organic and inorganic fluorides in its own reductive decomposition and show strong hydrophobicity. The reductive decomposition process of water is completely suppressed, Li metal and graphite have been used stably as negative electrode.

Besides directly resisting water molecules, there are also reports indicating that the coating layer is used to change the properties of electrode/electrolyte interface.^[38] For example, the HER catalytic activity of different coating layers on the surface of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) electrodes were studied (Figure 7).^[38c] It was found that Al_2O_3 has suitable hydrogen adsorption activity through DFT calculation, and electronic conductivity of Al_2O_3 is poor enough (Figure 7b). The Al_2O_3 layer of thickness in nanometer level was coated onto LTO electrode using atomic layer deposition. The coated LTO electrode can effectively reduce HER potential and has been used as aqueous battery-type electrode combined with regulation of electrolytes (Figure 7c–d).

In general, the different energy storage mechanisms and processes of various electrodes lead to significant differences in applicable regulation strategies. When designing and regulating the interfacial reaction from the perspective of electrode, the energy storage mechanism of electrode needs to be considered first. And the strategies of different electrodes can also be further combined to increase the operating voltage of aqueous hybrid capacitors under the premise that electrolyte is compatible.

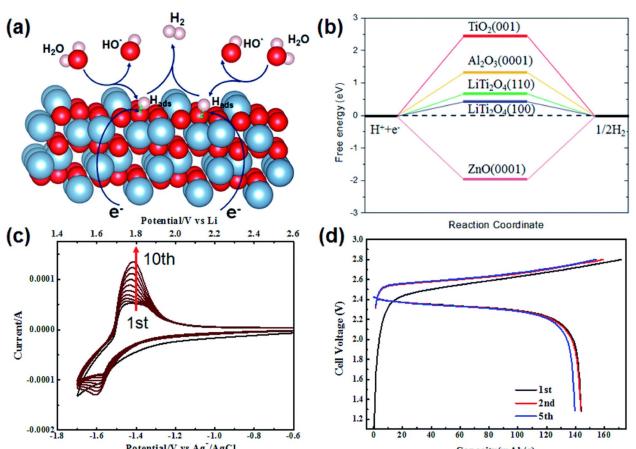


Figure 7. a) Schematic of HER process on electrode/electrolyte interfaces. b) Simulation results of the free energy of adsorption of hydrogen (ΔG_H) for the different surface coatings. c) Cyclic voltammetry scan of Al_2O_3 -coated LTO anodes at the scanning rate of 5 mVs^{-1} using activated carbon counter electrode and Ag/AgCl reference electrode. d) The voltage profile of the full cell using the Al_2O_3 -coated LTO anode and LiMn_2O_4 (LMO) cathode at 1 C current. Reproduced from Ref. [38c] with permission. Copyright 2020, Royal Society of Chemistry.

4. Regulation Strategies for Aqueous Electrolytes

For the regulation of aqueous electrolytes, the overall strategy is to change the electrochemical reaction behavior at electrode/electrolyte interface by regulating the composition of electrolytes. Similar to the regulation of electrodes, the regulated electrolyte can also suppress the electrolysis of water or prevent water molecules from contacting electrode. The effects such as changing the strength of the O–H bond,^[39] the interfacial ionization state^[40] or suppressing the reactivity^[39c,41] etc., can realize the expansion of electrochemical window of aqueous electrolytes. These strategies can be divided into three categories according to component characteristics: water-in-salt (WIS), asymmetric-pH and redox-enhanced electrolytes (Figure 8).

4.1. Water-in-Salt Electrolyte

Since it was proposed in 2015, WIS electrolyte has become hot field of aqueous electrolytes.^[39c] By dissolving large amount of electrolyte salt into water solvent, the obtained high concentration salt solution has different physical and chemical properties. The earliest developed and most studied WIS electrolyte is to dissolve up to 21 mols of LiTFSI into per kg of water (21 M) (Figure 9). The weight of electrolyte salt in the formed solution is much higher than that of water. Commonly, the first solvation shell of Li^+ is considered to contain 4 water molecules. But due to the lack of enough water, the maximum hydration number in this electrolyte is only 2.6. Therefore, unlike conventional aqueous electrolytes, most of water molecules in this WIS electrolyte are in hydrated state rather than free state.

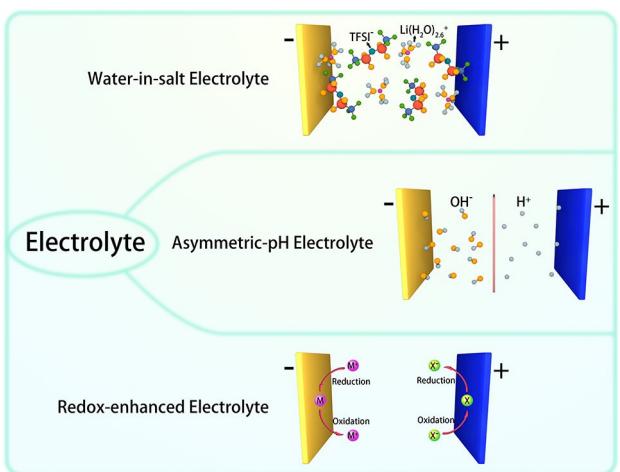


Figure 8. System design and mechanisms of electrolytes with wide electrochemical window.

The 21 m LiTFSI electrolyte can be described as large and soft quasi-ionic liquid composed of hydrated Li^+ and TFSI⁻, which means that it has completely different ion/molecular interaction and coordination state from conventional aqueous electrolytes.^[42] The specific mechanisms of electrochemical window expansion can be explained from three perspectives: (1) The change of main interaction in WIS electrolyte will strengthen the O–H bond in water molecules, making it more difficult for water to be electrolyzed. For example, the FT-IR of electrolytes with different LiTFSI concentrations was tested.^[42] The characteristic peaks of O–H bond stretching mode in high-concentration electrolyte were blue-shifted, confirming that bond energy and strength of O–H bond increased. But it is worth noting that the enhancement of O–H bond does not derive from the

hydration between Li^+ and water. On the contrary, as cation with strong Lewis acidity, when Li^+ coordinates with O in water molecule, the electron cloud between H and O move toward O, which lead to the weakening of O–H bond. This means that O–H bond is strengthened due to the interaction between TFSI⁻ and water.

- (2) The positive electrode has electrostatic repulsion to Li^+ during charging. In WIS electrolyte, most of the water molecules are in the solvation shell of Li^+ , and they will also receive electrostatic repulsion. Combined with the shielding effect of large-volume TFSI⁻, it can largely avoid OER of water molecules in contact with the positive electrode (Figure 10a).^[43]
- (3) For negative electrode, the effect of suppressing OER is mainly derived from the stable and dense SEI generated at the electrode/electrolyte interface, which is also the most prominent feature of WIS electrolyte. Since most of the water molecules are in coordination state and have lost the ability to dissolve SEI components, such as LiOH and Li_2CO_3 , this provides the possibility of SEI to exist stably in aqueous electrolytes. The concrete generation process of aqueous SEI was originally thought to be the result of the direct coordination between TFSI⁻ and Li^+ that increased the reduction potential of TFSI⁻, which results the reduction reaction of TFSI⁻ occurred before HER (Figure 9d–e).^[18b,39c] Nevertheless, there have been recent reports suggesting that this process is actually chemical process. The reduction product of water reacts with the electrophilic sulfur atom of TFSI⁻ through nucleophilic attack, thereby generating fluorinated SEI (Figure 10b).^[42,44]

Based on these mechanisms, the oxidation potential of aqueous electrolytes is increased, while the reduction potential is reduced. The electrochemical window was expanded up to 3.0 V (Figure 9a–c). Hereafter, various high-solubility salts and

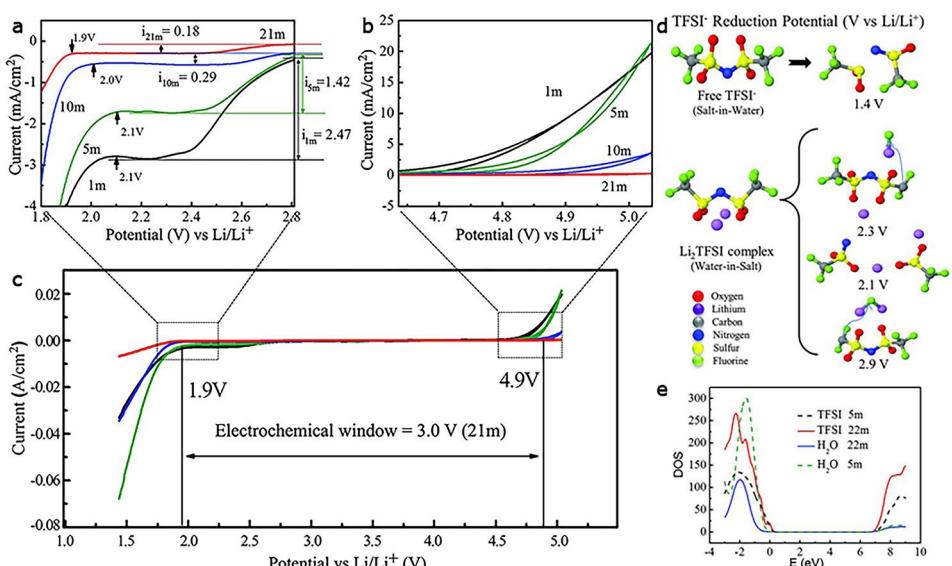


Figure 9. a, b, c) The electrochemical stability window of LiTFSI- H_2O electrolytes on nonactive electrodes. d) Predicted reduction potentials from quantum chemistry calculations. e) Projected density of states (DOS) for H_2O -LiTFSI electrolyte from DFT calculations. Reproduced from Ref. [39c] with permission. Copyright 2015, American Association for the Advancement of Science.

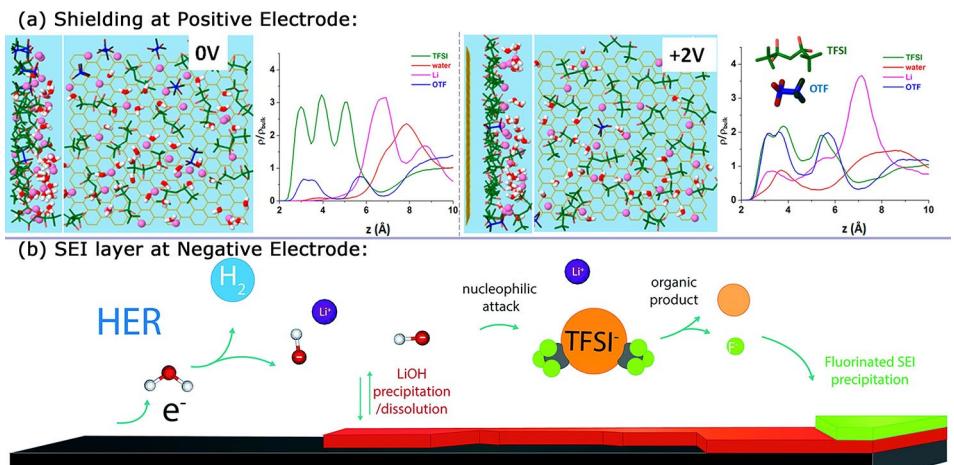


Figure 10. a) Cumulative atom number density profiles normalized by bulk density as function of distance from the electrode (z), snapshots of the interfacial layer at 0, and 2 V (vs the potential of zero charge), which shows the shielding effect of TFSI^- on water molecules at the positive electrode. Reproduced from Ref. [43] with permission. Copyright 2017, American Chemical Society. b) Schematic illustration of the formation of the SEI following “water reduction mediated mechanism” occurring at negative electrode in 20 m LiTFSI WIS electrolyte. Reproduced from Ref. [42] with permission. Copyright 2018, Royal Society of Chemistry.

co-dissolved salt systems were developed for the preparation of WIS electrolyte.^[37,45] The optimization of WIS electrolyte is still mainly to strengthen the O–H bond in water molecules, reduce the content of free water molecules, and generate a more stable SEI. Owing to the diversity of optional system components and interactions, different broadening mechanisms have also been proposed.^[39a,41a,46] Another promising development direction is the use of inexpensive, highly soluble inorganic salts instead of organic salts, which also show advantages in other aspects.^[45e,g,h] For example, 17 m NaClO₄ electrolyte has viscosity and ion conductivity far better than 21 m LiTFSI electrolyte, while maintaining wide electrochemical window, it can be used for 2.3 V high-rate carbon-based supercapacitor.^[45g] ZnCl₂ WIS electrolyte has also recently been found to be able to improve the energy storage capacity of porous carbon materials because Cl⁻ plays a decisive role in adjusting the desolvation of Zn ion clusters.^[45g,h]

WIS electrolyte also has applications in hybrid capacitors.^[45b,46–47] Due to the high solubility and low cost, lithium acetate (LiAc) was used as electrolyte salt to make up 13 m LiAc WIS electrolytes.^[47b] The high concentration of salt expanded the electrochemical window to 2.8 V. Oxygen-enriched crumpled graphene was selected as the capacitive electrode and Nb₁₈W₁₆O₉₃ as the battery-type electrode, 2.0 V aqueous hybrid capacitor was assembled. 1-ethyl-3-methylimidazolium (EMIM)-TFSI and LiTFSI together in water were dissolved, and the “water in salt/ionic liquid” electrolyte can exhibit wide electrochemical window of 3.8 V and be used to assemble stable Nb₂O₅||AC hybrid capacitors.^[46] Because the EMIM⁺ with large volume can be adsorbed on negative electrode to prevent water molecules from contacting the electrode, the reduction potential can be lowered more than the conventional WIS electrolyte that only SEI works.

Besides changing the type and proportion of salts, the organic additives are another promising improvement strategy as they can effectively optimize the interaction between

components or provide unique functions.^[48] Polyethylene glycol (PEG) as molecular crowding agent to replace the hydrogen bonds between water molecules in WIS electrolyte was proposed. The newly formed weak hydrogen bonds between PEG and water molecules can reduce the negative impact of hydrogen bonds on O–H bond, and the strength of O–H bond will be improved. Compared with original WIS electrolyte, the electrochemical window of this electrolyte is further expanded up to 3.2 V. When urea is used as additive, by adjusting the coordination state between urea molecules and Li⁺, it can be decomposed into SEI at both positive and negative electrodes, which will expand the electrochemical window.^[41a] Tetraethylene glycol dimethyl ether (TEGDME) as an additive can improve the SEI generated at negative electrode, thereby further reducing hydrogen evolution potential of water.^[49]

Although WIS electrolyte can meet the demands of hybrid capacitors for electrochemical window and energy density, it also shows obvious defects in viscosity and conductivity. In order to achieve high solubility, the anion of selected salt is usually bulky organic anion. The increase in salt concentration leads to an increase in electrolyte viscosity, which thereby reduces ionic conductivity. In such solution environment, it is difficult for bulky anions to enter small micropores, which causes loss of specific capacitance for EDL capacitive electrodes. The generated SEI can also plug the micropores to prevent ion adsorption, which also affects the capacitance.^[50] Therefore, designing low-viscosity WIS electrolyte and choosing suitable capacitive electrode to match it will be essential when using WIS electrolyte for hybrid capacitors.

4.2. Asymmetric-pH electrolytes

Although it is theoretically difficult to increase the oxidation potential while reducing the hydrogen evolution potential by merely adjusting the overall pH, the asymmetric pH at positive

and negative electrodes constructed by system design has become stable and effective method to expand electrochemical window. The principle of this strategy is to use ion conductive membranes, through which H^+ or OH^- cannot pass to divide the electrolytes into positive area and negative area. Alkaline electrolyte is used in negative area to suppress the occurrence of HER, while acid or neutral electrolytes used in positive area will maintain the high OER potential of water. Since H^+ and OH^- cannot pass through ion conductive membrane, pH of two areas can be kept different, thereby simultaneously reducing reduction potential and maintaining high oxidation potential.^[40,51] For example, bipolar membranes that simultaneously inhibit H^+ and OH^- shuttles can be used to construct acid-alkali asymmetric electrolyte.^[51a,b] Only the shuttle of K^+ and SO_4^{2-} maintains the charge balance of two areas while keep the pH constant, and the electrochemical window will be expanded to more than 3 V.^[51b]

Even tough asymmetric-pH electrolyte is also an effective strategy for constructing aqueous high-voltage hybrid capacitors,^[51e,f] but it should be noted that the selection and matching of positive electrodes, negative electrodes and the electrolyte on each area is critical. For example, when commercial materials are used to assemble hybrid capacitors, alkaline electrolytes can be used in the negative electrode area to suppress HER. Nevertheless, it is still not enough to be applied to commercial battery negative materials with low charge and discharge potential, such as LTO and graphite. In contrast, the capacitive electrode is good choice for the negative electrode, and commercial LMO with redox potential close to OER potential can be selected as the cathode material. However, LMO will dissolve under acidic environment.^[52] Therefore, while matching the positive and negative materials, it is also necessary to match electrode materials and their corresponding pH environment. For example, the alkaline-neutral electrolyte constructed with K^+ conductive film for aqueous high-voltage hybrid capacitors was designed (Figure 11).^[51e] Biomass carbon is used as capacitive negative electrode to obtain good capacitive performance in alkaline electrolyte. While on positive side, lithium manganate and neutral electrolyte are matched to achieve stable charging and discharging, aqueous hybrid capacitor with a voltage of 2.3 V was assembled.

4.3. Redox-Enhanced Electrolyte

Redox-enhanced electrolyte is the type of electrolyte with reversible redox active ions. For electrodes, the ions in conventional electrolytes mainly store charge through one of the mechanisms of adsorption/desorption, insertion/extraction and deposition/dissolution. But the redox active ions added in redox-enhanced electrolyte will occur reversible redox reactions based on adsorption/desorption. Redox active ions do not participate in the redox reactions of electrode materials. The mechanism is similar to that of deposition/dissolution of Li, Zn and other metal ions, but the stability, degree of reaction and application are quite different.^[53] For the cell with redox-

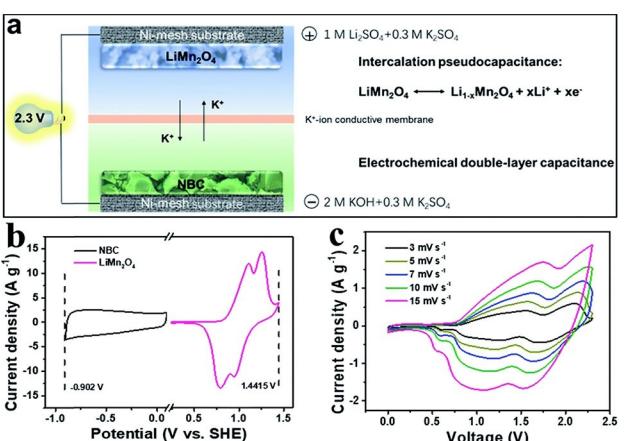


Figure 11. a) Structural illustration and energy storage mechanism of the as-fabricated nitrogen-rich biomass carbon (NBC) || LMO hybrid capacitor with the alkaline-neutral electrolyte. b) CV curves (vs. SHE, 25 °C) of NBC and LMO electrodes in 2 M KOH and 1 M Li_2SO_4 aqueous electrolyte solutions at scan rate of 10 mV s^{-1} , respectively. c) CV curves of the hybrid capacitor with the alkaline-neutral electrolyte between 0 and 2.3 V at different scan rates. Reproduced from Ref. [51e] with permission. Copyright 2018, Royal Society of Chemistry.

enhanced electrolyte, redox active ions are first adsorbed on the surface of electrode during the charging process to form electric double layers. As the electrode potential exceeds their redox reaction potential, the redox active ions are oxidized to a higher valence state or reduced to a lower valence state. When discharging, an opposite process takes place to release charges. Redox-enhanced electrolyte is therefore usually used for EDL electrodes with high specific surface area and introduces faradaic redox reaction to increase capacity. Variety of ions have been studied in redox-enhanced electrolyte, such as viologen (V) di-cation, halogen (Cl, Br, I) anions, transition metal (Fe, Cu, V, Cr) cations, tetramethylpiperidine-N-oxide (TEMPO) cation, $[Fe(CN)_6]^{4-}$, etc.^[54] In addition to capacity-enhancing function, the redox active ions with redox potentials close to the electrolysis potential of water can expand electrochemical window of electrolyte. The mechanism is similar to the regulation of pseudocapacitive electrode, which can be attributed to the faster kinetics compared with HER or OER. Therefore, redox-enhanced electrolyte is also commonly used to construct high-voltage aqueous electrical energy storage devices. For example, Br^- and $[Fe(CN)_6]^{4-}$ can be used as the redox active ions for positive electrode. In a suitable system, their oxidation potential is slightly lower than OER potential, which can effectively inhibit the OER of water.^[55] The redox reaction of methyl viologen di-cation (MV^{2+}), ethyl viologen di-cation (EV^{2+}), heptyl viologen di-cation (HV^{2+}), etc. at negative electrode will suppress HER of water.^[54b]

In addition to its own advantages, redox-enhanced electrolyte has more profound significance for hybrid capacitors. When assembling hybrid capacitor, the total capacity of positive and negative electrodes needs to be the same, but the mass specific capacity of capacitive electrode has large gap compared with battery-type electrode.^[56] In order to make full use of the capacity of the battery-type electrodes, capacitive

electrodes with large mass proportion are usually required, therefore, the energy density of hybrid capacitors is limited. The redox activity into EDL capacitive electrode to enhance its capacity can effectively reduce the difference in mass specific capacity between positive and negative electrodes, which will balance the mass ratio of two electrodes and greatly improve the total energy density.^[57] Combined with the ability of redox-enhanced electrolyte to expand electrochemical window, the energy density of hybrid capacitors can be greatly improved.^[41b,57b,58] For example, the potential fringe strategy to improve electrochemical window and energy density of hybrid capacitors was proposed (Figure 12).^[41b] $[\text{Fe}(\text{CN})_6]^{4-}$ was selected as the redox active ions to enhance the capacity of reduced graphene oxide (rGO) cathode, and TiO_2 , which can perform rapid Li^+ insertion/extraction, was used as the anode material (Figure 12a). The rapid kinetics of $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ redox reaction inhibit the OER reaction of water and combine with the TiO_2 electrode to suppress HER. As a result, the electrochemical window and operating voltage of hybrid capacitor with alkaline electrolyte was expanded to 2 V, and the energy density was improved greatly (Figure 12b–c).

However, it should be noted that although redox-enhanced electrolyte can effectively expand the electrochemical window of aqueous hybrid capacitors and increase energy density, it still has the limitations. One of them is the inherent defect of redox-enhanced electrolyte. The dissolved redox active ions are usually only adsorbed on the surface of the electrode under static electricity. The charging and the rest process after charging is completed, part of the charged redox active ions will escape from electrode surface and be back into electrolytes. The loss of charged ions and their discharge on the opposite electrode cause rapid self-discharge and reduce the coulombic efficiency. Therefore, it is usually necessary to adopt strategies, such as electrostatic effects^[54b] and physical

confinement^[59] to suppress self-discharge. Besides, owing to the faradic redox reaction on capacitive electrode, the energy storage mechanism has changed, which will affect the rate performance of EDL capacitive electrode and the overall power density of hybrid capacitors. In addition, different redox active ions have different requirements for the pH of electrolytes. When constructing the corresponding aqueous hybrid capacitors, it is necessary to comprehensively consider the charge and discharge potential of redox active ions and battery-type electrode, the pH of electrolytes, and the resistance of pseudocapacitive or battery-type electrode to electrolyte.

The above strategies are mainly to adjust the composition of electrolyte to regulate electrode/electrolyte interfacial reaction. In fact, the physical form of electrolyte is also factor that affects electrode reaction. The use of elastic crosslinked hydrated polymer chains and water to prepare hydrogel electrolyte is typical method to change the physical form of the electrolyte.^[60] The advantages of hydrogel electrolytes are not only reflected in the high ionic conductivity and dimensional stability of solid. Because water is absorbed and trapped in polymer framework, the migration of water to electrode/electrolyte interface is hindered, which prevents the electrolysis of water to a certain extent and expands electrochemical window.^[61] In addition, the regulation strategies for electrolyte can also be combined with the hydrogel electrolyte to further expand electrochemical window and optimize the energy storage device.^[62]

In summary, the regulation of electrolyte is essentially to control interfacial reactions by adjusting chemical composition directly or indirectly. Ionization balance, ion coordination state, redox activity and hydrogen bond structure can be changed to control the accessibility and reactivity of water at electrode/electrolyte interface. The regulation of electrolyte can further match with the regulation of electrode on the premise of being compatible with electrode, to increase the operating voltage of aqueous hybrid capacitor.

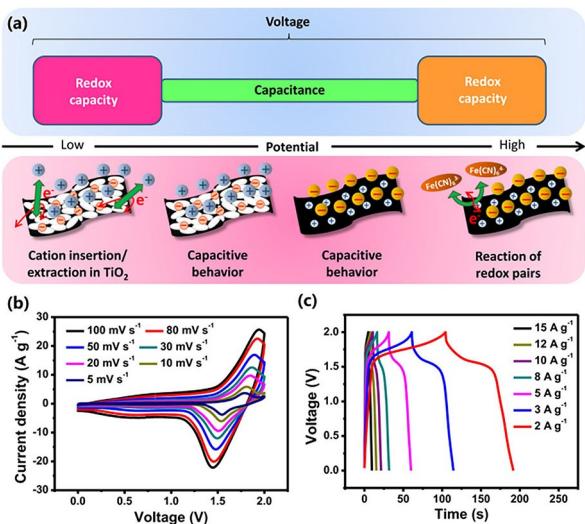


Figure 12. Electrochemical performances of the hybrid capacitor based on $\text{TiO}_2@r\text{GO}$ film anode and rGO film cathode in $\text{LiOH}/\text{K}_4\text{Fe}(\text{CN})_6$ electrolyte: a) coupling of the two fast potential-fringe redox reaction; b) CV curves at various sweep rates; c) galvanostatic charge/discharge curves. Reproduced from Ref [41b] with permission. Copyright 2019, Wiley-VCH.

5. Construction of High-voltage Aqueous Hybrid Capacitors

In addition to adjusting the interfacial reactions from the perspectives of electrodes and electrolytes, the key factor to the application of high-voltage aqueous hybrid capacitors is the design of entire electrochemical system. Due to varied HER and OER potentials of different electrodes, the asymmetric design of hybrid capacitors yields them higher operating voltage. Building on the existing high operating voltage, the interface regulation will further expand electrochemical window and enable the assembled devices to have operating voltage far beyond that of conventional aqueous hybrid capacitors (Figure 13). It requires to pay more attention to the matching and compatibility of each component. For example, priority is given to the stability of electrode at the current pH value. The matching between the reaction potentials of redox additive and electrode, as well as the matching between the

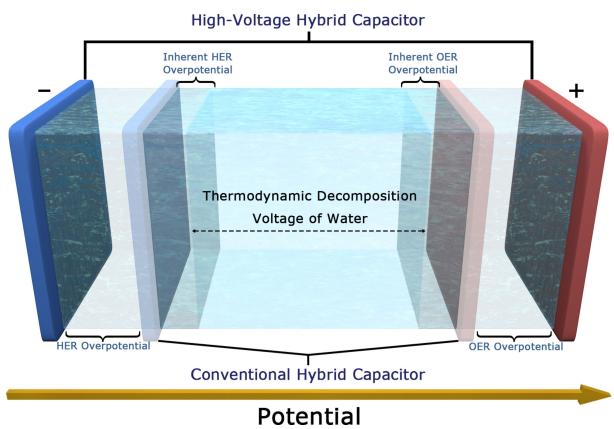


Figure 13. Construction of high-voltage aqueous hybrid capacitors with interfacial reactions regulation strategies.

capacity and rate performance of different electrode cannot be ignored. The examples of high-voltage aqueous hybrid capacitors and their corresponding regulation components are summarized in Table 2. It is for sure that electrochemical system design is not the only way to optimize the voltage and energy density of energy storage devices. Strategies such as electrochemical charge injection and surface charge control that can effectively control electrode potential have also proven to be feasible to better utilize electrochemical window and increase voltage and energy density.^[56a,63]

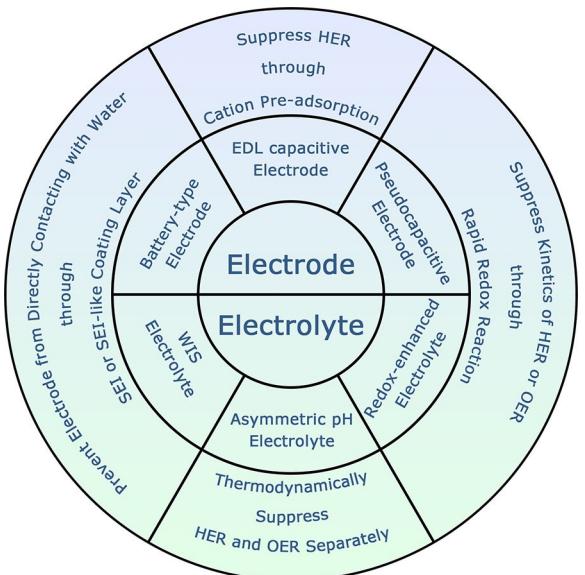


Figure 14. Summary of different regulation strategies and corresponding mechanisms for electrode/electrolyte interfacial reactions from the two aspects of electrode and electrolyte.

6. Summary and Perspective

To bridge the between commercial secondary batteries and EDL capacitors, hybrid capacitors combine the advantages of them and demonstrate great potentials. It is clear that the

Table 2. Summary of high-voltage aqueous hybrid capacitors and corresponding regulation strategies (in bold).

| Positive electrode | Negative electrode | Electrolyte | $V_{\max}^{[a]}$ [V] | $E_{\max}^{[b]}$ [Wh kg ⁻¹] | Ref. |
|--|---|---|----------------------|---|-------|
| Carbon-coated Mn ₃ O ₄ Co ₃ O ₄ /ACC ^[c] @rGO | Graphene Aerogel (Na ⁺ adsorption) ACC@RGO | 1 M Na ₂ SO ₄ | 2.7 | 110.4 | [27e] |
| Na _{0.25} MnO ₂ Nanosheets | Porous Carbon (Na ⁺ adsorption) | 2 M Li ₂ SO ₄ + 0.1 M CoSO ₄ | 2.2 | 99 | [27a] |
| K _{0.6} MnO ₂ | Holey Carbon (K ⁺ adsorption) | 1 M Na ₂ SO ₄ | 2.7 | 61.1 | [27c] |
| Li ₄ Mn ₅ O ₁₂ Nanoflakes | AC | 1 M KTFSI | 2.4 | 52.8 | [27b] |
| AC | Mo _{0.1} W _{0.9} O _{3-x} / CNTs ^[d] | 2 M Li ₂ SO ₄ | 2.2 | 78 | [64] |
| AC | Protected Li _x C ₆ | 1 M Li ₂ SO ₄ | 2 | 111.6 (μWh cm ⁻²) | [33b] |
| AC | Nb ₂ O ₅ | 3.7 | [65] | | |
| Crumpled Graphene Li ⁺ -intercalated MnO ₂ | Nb ₁₈ W ₁₆ O ₉₃ Interwoven Carbon Network | LiTFSI/H ₂ O/ (EMIM-TFSI) _{2,0} | 2.8 | 51.9 | [46] |
| Polyimide VO ₂ | Porous Carbon Microspheres | 13 m LiAc | 2 | 41.9 | [47b] |
| LiMn ₂ O ₄ Nanorods | AC | 21 M LiTFSI + 1 M Li ₂ SO ₄ | 2.8 | 55.7 | [45b] |
| CNTs | Nitrogen-rich Biomass Carbon | 17 m NaClO ₄ | 2 | 65.1 | [47a] |
| rGO | Zn metal | 8 m NaTFSI | 2.4 | [47c] | |
| LSG ^[e] | TiO ₂ @rGO | (+) 1 M Li ₂ SO ₄ / 2 M KOH (-) | 2.3 | 50 | [51e] |
| | LSG/Fe ₃ O ₄ | (+) 0.5 M H ₂ SO ₄ / 3 M KOH (-) | 2.4 | [51f] | |
| | | 1 M LiOH/ | 2 | 70.4 | [41b] |
| | | 0.2 M K ₄ Fe(CN) ₆ | | | |
| | | 1.0 M Na ₂ SO ₄ + 0.025 M K ₃ Fe(CN) ₆ | 1.8 | 121 | [55b] |

[a] V_{\max} : Maximum voltage. [b] E_{\max} : Maximum energy density. [c] ACC: activated carbon cloth. [d] CNTs: carbon nanotubes. [e] LSG: laser-scribed graphene.

development and practical application of hybrid capacitors can be a step forward when safer and cheaper aqueous electrolytes can be used for hybrid capacitors, which solves the shortcomings of narrow electrochemical window. This review summarizes the currently available strategies for expanding the electrochemical window of aqueous hybrid capacitors. Comparing with secondary batteries and electrochemical capacitors, which have been studied extensively, there are relatively few research on emerging hybrid capacitors. Most of current research on electrochemical window of aqueous electrolytes are based on specific type of device. However, it is obvious that as combination device, an overview of strategies proposed for every electrode have the potential of being applied to hybrid capacitors. A more complex electrochemical behavior of hybrid capacitors leads to challenge when these strategies are applied to the design of high-voltage aqueous hybrid capacitors. Regarding to these possible problems, a brief summary can be made as follow:

- (1) For EDL capacitive electrodes, an effective strategy is to increase the HER overpotential on electrode surface by cation pre-adsorption. It has only been theoretically proved that the pre-adsorption of Na^+ and K^+ on heteroatom-doped carbon can increase HER overpotential, thereby expanding the electrochemical window. The mechanism and specific changes of electrochemically treated carbon need to be further studied. Different effects of varied metal ions on HER are also required to be clarified. In addition, considering that emerging aqueous hybrid capacitors such as Zn-ion capacitors and Mg-ion capacitors usually use EDL capacitive electrodes as positive electrodes, the regulation strategy of EDL capacitive electrodes for suppressing OER is also worthy of attention. For example, by introducing extra positive charges to carbon materials to adsorb anions, whether it can suppress the OER of water is a direction that can be explored.
- (2) For pseudocapacitive electrodes, the main strategy is to introduce rapid redox reaction near water electrolysis potential to compete with HER or OER. The rapid redox reaction can inhibit HER or OER from the perspective of kinetics. As the charging process finishes, whether electrode that no longer reacts can still inhibit HER or OER from the perspective of kinetics needs to be considered. In addition to the redox reaction, it is also an effective strategy to directly change the overpotential of HER or OER overpotential on electrode surface through the adjustment of interfacial chemical structure, but there is still a lack of mechanism understanding to guide corresponding structure design.
- (3) For battery-type electrodes, one of the most effective strategies is to coat electrode surface with SEI-like ion-conductive layer to prevent electrode from directly contacting with water, which can fundamentally avoid the electrolysis of water. However, the influence of thicker coating layer on the polarization of hybrid capacitors needs to be considered. It is less meaningful for hybrid capacitors to increase energy density at the cost of losing the power density. The use of the expensive ceramic solid electrolytes will also lead to greatly increased costs. Besides, using nano-coatings with higher HER or OER overpotential to modify electrode surface is strategy with development and application potential. But at present, this strategy also lacks mechanism understanding to design the composition of coating layer and universal coating method.
- (4) For WIS electrolyte, the diversity of optional salts and additives leads to complex ion-solvent coordination state. More electrochemical window expansion mechanisms have also been further proposed, including but not limited to the formation of water-stable SEI, increasing the strength of O–H bond and shielding water molecules by ions. Overall, the issue that needs to be considered is the performance of capacitive electrodes in WIS electrolytes. Both the high concentration of salt and the large volume of anions will affect the kinetic process of hybrid capacitors. Especially for EDL electrodes, large anions may not be able to freely enter and leave the micropores, which will affect the capacitance and rate performance. SEI may also block the micropores. Therefore, it is necessary to choose a suitable electrode-electrolyte combination and to develop high-performance low-viscosity electrolyte to solve these issues.
- (5) For asymmetric-pH electrolyte, the fundamental mechanism is to maintain different pH values on both electrode/electrolyte interfaces to change interfacial reactions. On each side, the composition of asymmetric-pH electrolyte is the same as that of a conventional aqueous electrolyte. But overall, it has achieved the compatibility of acidic and alkaline electrolytes in the same electrochemical system through the ion conductive membrane. And from a thermodynamic viewpoint, HER at the positive electrode and OER at the negative electrode are simultaneously suppressed. Since battery-type electrodes and pseudocapacitive electrodes that may be used are less chemically stable than carbon, the resistance of electrode materials to electrolyte needs to be considered. Compared with other electrolytes, the system design of asymmetric-pH electrolyte requires more consideration.
- (6) For redox-enhanced electrolyte, the mechanism is to introduce a rapid redox reaction to inhibit the kinetics of HER or OER. Therefore, it needs to consider whether HER and OER can be suppressed all the time during the reaction. In addition, inherent defects such as the shuttling of redox additives should also be considered during the system designing.
- (7) For the construction of high-voltage aqueous hybrid capacitors, the key factor is to make use of the asymmetric design for hybrid capacitors. According to its wide electrochemical window, various regulation strategies of interfacial reactions should be further introduced into hybrid capacitors. It is also necessary to consider the compatibility and matching of electrodes, electrolytes, and various strategies. Reasonable designs can maximize the operating voltage to achieve high energy density and safe high-voltage aqueous hybrid capacitors.

In longer term, the development of high-voltage aqueous hybrid capacitors is based on the understanding of water electrolysis process. The effect of different strategies is essentially to regulate the electrode/electrolyte interfacial reactions through electrode structure design or electrolyte composition design directly or indirectly. Targeted strategies make HER or OER be suppressed from the perspective of kinetics or thermodynamics (Figure 14).

The study of interfacial reactions regulation strategies to expand electrochemical window is also conducive to deepening the understanding of HER and OER process, which in turn has inspiring significance for the mechanism exploration and structural design in the fields of electrocatalysis, photocatalysis, metal-air battery and fuel cells.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: high voltage · aqueous hybrid capacitors · regulation strategies · interfacial reactions · electrochemical window

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