Recent advances in materials and device technologies for aqueous hybrid supercapacitors

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ABSTRACT Aqueous hybrid supercapacitors (AHSCs) offer potential safety and eco-friendliness compared with conventional electrochemical energy storage devices that use toxic and flammable organic electrolytes. They can serve as the bridge between aqueous batteries and aqueous supercapacitors by combining the advantages of high energy of the battery electrode and high power as well as long lifespan of the capacitive electrode. Over the past few decades, extensive research efforts have been devoted to developing advanced materials and fascinating device architectures for AHSCs. However, further development related to the compatibilities between the battery-type electrode and capacitive electrode remains stagnant mainly due to discrepancy encountered in terms of reaction kinetics and capacity. This review focuses on the recent progress made in the field of AHSCs *via* elucidating the main concepts on the design of battery and capacitive electrodes and emerging electrolytes. In particular, ingenious AHSCs that possess either better flexibility toward materials selection or better device functionality such as those with “dual-ion” energy storage mechanism and non-polarity feature are also discussed. Recent advances and unresolved issues in multivalent ion hybrid devices (in particular, zinc-ion AHSCs) are further outlined. Finally, future research directions and challenges for AHSCs are presented, which are anticipated to deliver higher energy and demonstrate greater multifunctionalities for more breakthrough technology applications.

Keywords: aqueous hybrid supercapacitors, electrode materials, electrolytes, device technologies

INTRODUCTION

Achievement of secure and sustainable energy storage on large scale is one of the greatest scientific and societal challenges of this era. Electrical energy sources (EESs) as potential sustainable energy supplies play a vital role in our daily life because of the extensive use of various mobile electronic devices [1–3]. Electrochemical energy storage devices such as Li-ion batteries (LIBs) [4], Li-S batteries [5], Li-O₂ batteries [6], and supercapacitors (SCs) [7–9] are high-efficiency EESs attracting tremendous interests in recent years, which have greatly reduced

our dependence on fossil fuels [4,5]. Among them, LIBs have been widely used in portable electronics and are almost ready for emerging application in the field of electric/hybrid vehicles [4]. With their extended uses in different fields, the safety issues resulting from the use of flammable organic electrolytes and the growing cost of limited lithium sources have become more critical. Aqueous batteries using simple aqueous electrolytes are a fascinating alternative to solve the safety issue of organic electrolyte-based batteries [10]. To reduce the cost of LIBs, replacing lithium-based electrodes with sodium (Na)- and potassium (K)-based ones and the constructions of Na- and K-ion batteries have also emerged [11–15].

In specific application fields or cases that require energy storage devices with high power and extremely long lifespan, batteries are generally not qualified as they are difficult to be fully charged in short time and basically subjected to volume changes during each cycle. In contrast, SCs fulfill these requirements even though their energy density is inferior to that of batteries [16,17]. Since the discovery of electrical double layer capacitor (EDLC) by Helmholtz in 1879 [18], the charge storage process based on pure electrostatic charge accumulation at the electrode/electrolyte interface and the electrode materials for EDLC have been extensively investigated. An alternative charge storage mechanism for SCs, that is pseudocapacitance *via* fast and reversible surface redox processes or redox reactions in quasi-two-dimensional (2D) planes in bulk crystal lattice, was proposed later. Since then, pseudocapacitive materials have been developed for tens of years [19–23]. Noteworthy, owing to the fast-charging ability and high power, SCs are typically employed as backup power sources to complement batteries. By using low-cost and nonflammable water-based electrolytes, SCs are also intrinsically safe, alike aqueous batteries [24]. Consequently, great research attempts have been made to develop aqueous SCs and related energy storage devices in the past few decades [18,24,25].

As one of the key outcomes, aqueous hybrid SCs (AHSCs) that consist of one capacitive electrode and one battery-type electrode emerged at a historic moment by virtue of complementary advantages of batteries and capacitors (Fig. 1) [26–28]. By considering the charge storage mechanisms of two electrodes, the general working principles of AHSCs can be elucidated as follows [29,30]: during charging and discharging

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Figure 1 Illustration of the device structure, charge storage mechanism, materials design concepts of AHSCs. “A (M)” and “B” are ions involved in charge storage process for capacitive electrode and battery-type electrode, respectively.

process, ions in electrolytes move to electrodes. The capacitive electrode typically undergoes reversible adsorption/desorption of ion (A) at the electrode/electrolyte interface or rapid surface/near-surface Faradaic reaction (M) to store charges; however, the other battery-type electrode suffers bulk redox reactions (B ion involved) with charge transfer across the electrode/electrolyte interface. According to the above-stated fundamentals, the capacitive electrode with fast electrochemical kinetics can offer rapid energy uptake and delivery. Further, the battery-type electrode with intensive redox activity can provide more energy, thus ideally endowing AHSCs with both high power and energy density. In particular, the asymmetric device configuration with different charge storage mechanisms of electrodes can increase the hydrogen and oxygen evolution overpotentials in aqueous electrolytes. As a result, the device voltage thereby extends beyond 1.5 V and even up to ~2.0 V (intrinsic electrochemical stability window of water is merely ~1.23 V) [14,31]. Therefore, AHSCs are expected to deliver larger amount of energy than conventional aqueous SCs and superior power performance to aqueous batteries. Successful examples were demonstrated using a Faradaic conversion positive electrode ($\text{PbO}_2/\text{PbSO}_4$ in aqueous H_2SO_4 or $\text{NiOOH}/\text{Ni(OH)}_2$ in aqueous KOH) and a capacitive activated carbon (AC) negative electrode [32]. In recent years, various other types of aqueous AHSCs such as aqueous Li/Na/K-ion capacitors (ALICs, ASICs, and APICs, respectively) and redox AHSCs have been proposed and devel-

oped. Moreover, a wide spectrum of new electrode materials have been utilized to achieve innovative electrode couples [11,14,33–36]. Unfortunately, to boost the performance on device level and widen the application fields of AHSCs, critical challenges are still encountered in understanding the energy storage mechanism of new hybrid systems, engineering the surface chemistry/structure/morphology of electrode materials, regulating the electrolytes, and designing stable interfaces within the device.

By using anode and cathode with different energy storage mechanisms, it generally becomes more difficult to realize perfect charge and kinetics balance between the two electrodes in AHSCs. First, the intercalation/deintercalation or conversion kinetics in battery-type electrode cannot match well with the capacitive electrode, which deteriorates the practical rate capacity and cycling stability of the hybrid devices [37–39]. Thus, strategies to deal with this issue lie in developing advanced battery-type electrodes with specific components, micro-nano-structures, or electronic and crystal structures to promote the charge transfer at the interfaces and electron/ion transport in the solid electrodes [40–43]. The unsatisfactory specific capacitance of the capacitive electrodes is another factor that limits the practical performance of AHSCs; this is attributed to the fact that the capacitive electrode should generally be much thicker and heavier than battery electrode to achieve the charge balance, which is inconvenient for device assembly and not beneficial to

volumetric/gravimetric performance. The increased weight and volume may also lead to limited electrolyte/electrode interfacial contact that can restrict the materials utilization and rate performance. Therefore, to address this issue, the major challenge is to boost the specific capacitance of the capacitive electrodes. Notably, this can be achieved by optimizing the pore structure/size, tuning the surface chemistry, and doping of EDLC materials (capable of introducing pseudocapacitive effect), or by directly using high-capacity pseudocapacitive materials [44–47]. The difference in cycling stability between battery-type electrode and capacitive electrode is also a key to design high-performance AHSCs. In addition to the matching consideration of positive and negative electrodes, the energy density of AHSCs has been of another concern in the SC field. Owing to water electrolysis involving H_2 and O_2 evolution, the voltage window of AHSCs is generally limited to 2.0 V despite its asymmetric configuration [48]. Thus, according to the equation $E = 1/2CV^2$ (where C and V are the specific capacitance and operating voltage of the device, respectively), the energy density of AHSCs is much lower than that of conventional SCs. Fortunately, recent advances have indicated that the V can be significantly widened *via* designing advanced electrolyte, electrode, and robust electrode/electrode interface [49]. To efficiently power flexible and wearable electronics, afford miniaturized energy delivery or harvest with high power capabilities for Internet of Things, significant research efforts have also been devoted to developing thin-film flexible AHSCs using quasi-solid-state/gel electrolytes and flexible/bendable current collectors [50–52]. Such functionality design into device was also combined with electrode engineering to construct new types of AHSCs, which demonstrates promising potential in some specific application scenarios [7,51,53]. Despite the existence of some related reviews and perspectives [7,16,18,19,22,25,26], advances on new concepts of designing electrode, electrolyte, and device of AHSCs have not been well outlined.

In this review, an attempt was made to briefly summarize the key performance improvement strategies for AHSCs in terms of the design of advanced battery-type and capacitive electrodes and the optimization of electrolyte (e.g., concentration regulation and hydrogel electrolyte design). The ingenious design of some emerging AHSC devices, such as “dual-ion” AHSC and non-polarity AHSC are also expatiated, which are assembled with novel device structure and operated based on interesting charge storage process. Furthermore, recent advances and unresolved issues in multivalent ion hybrid devices, in particular, in the most popular zinc-ion AHSCs are discussed herein. Finally, perspectives on the challenges and opportunities for developing future AHSCs are presented with the objective of maximizing the amount of stored energy and the speed of energy delivery as well as enriching the device multifunctionalities.

DESIGN OF BATTERY-TYPE ELECTRODES IN AHSCs

As one of the key components in AHSCs, the battery-type electrode has been focused upon in recent decades for the sake of alleviating the kinetics discrepancy between the electrode and capacitive counterpart to improve the cycling performance and increase the energy density of device at high power. Till date, several approaches have been developed to realize the above-mentioned objectives *via* promoting the electron transport and ion diffusion within solid electrode and accelerating the charge

transfer at the interface. These approaches are as follows: (1) micro-nanostructures manipulation, such as growth of ordered arrayed electrode architecture and sophisticated coating of pristine materials with stabilizing layer, conductive layer, or energy-contributing species; (2) electronic and crystal structures tuning (solid-solution design, intrinsic defects, doping, etc.); and (3) searching for new battery-type materials with rapid electrochemical kinetics for AHSCs (Fig. 1, right side).

$\text{Li}^+/\text{Na}^+/\text{K}^+$ storage electrodes

Similar to the use in non-AH devices, $\text{Li}^+/\text{Na}^+/\text{K}^+$ storage materials such as intercalation/insertion compounds have also attracted significant research interest as battery-type electrode materials for AHSCs. Considering the standard redox potentials of alkali ion storage in these materials (3.3–4.5 V *versus* Li^+/Li ; ca. 0–1.2 V *versus* Ag/AgCl) and overpotentials during practical reactions, actually quite a few cathodes in non-aqueous systems can be utilized directly in AHSCs without the interference from apparent oxygen evolution reaction. These cathode materials include Mn-based oxides (e.g., LiMn_2O_4 [54], $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{O}$ [55], $\text{Na}_4\text{Mn}_9\text{O}_{18}$ [56], and K_xMnO_2 [57,58]), polyanionic compounds (e.g., LiFePO_4 [59] and $\text{Na}_2\text{VTi}(\text{PO}_4)_3$ [60]), Prussian blue analogs (PBAs) (e.g., $\text{Na}_2\text{NiFe}(\text{CN})_6$ [61] and $\text{K}_x\text{Fe}_y\text{Mn}_{1-y}[\text{Fe}(\text{CN})_6]_w \cdot z\text{H}_2\text{O}$ [62]), and other layered compounds (e.g., $\text{Na}_{2/3}\text{Ni}_{1/4}\text{Mn}_{3/4}\text{O}_2$ [63] and LiCoO_2 [64]). In contrast, many anode materials used for non-AH devices have much lower redox potentials beyond hydrogen evolution and are impossible to be employed in AHSCs. Therefore, relatively few anode materials, such as Ti-based polyanionic compounds ($\text{LiTi}_2(\text{PO}_4)_3$ [65] and $\text{NaTi}_2(\text{PO}_4)_3$ [66]), carbonyl-based organic compounds (poly-(naphthalene-4-formyl ethylenediamine [67]), and vanadium-based oxides (V_2O_5 [68] and $\text{Na}_2\text{V}_6\text{O}_{16} \cdot n\text{H}_2\text{O}$ [69]) are available. Several comprehensive reviews have discussed the cathode and anode materials for Li^+/Na^+ AHSCs [14,26,27,70,71]. Although morphological characterization and micro/nano-structure engineering have been widely investigated toward battery-type electrodes for boosting the redox kinetics and cycling stability, other promising strategies such as electronic structure tuning *via* doping or formation of solid solution have also been proposed and developed in recent years [55,66,72,73].

A good example was demonstrated by fabricating Ni-Mn-O solid-solution cathode for ALICs [55]. With similar radius to 3d-metal elements and the same NaCl crystal structure to 3d-metal monoxides, MnO easily forms solid solutions with the introduction of other metal ions such as Ni^{2+} [74]. In the study, a unique MnO-based 3d-metal monoxide solid-solution cathode ($\text{Ni}_{0.25}\text{Mn}_{0.75}\text{O}$) was synthesized directly on current collector substrate with a nanoprism array architecture (Fig. 2a). The synthesis process involved the direct hydrothermal growth of Ni-Mn carbonate nanoprisms and subsequent thermal decomposition into solid-solution oxide during annealing. Inset of Fig. 2b illustrates that the $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{O}$ electrode exhibits two pairs of redox peaks with both higher current densities and lower polarizations compared with the pristine MnO electrode in the cyclic voltammogram (CV) curves. In-depth electrochemical impedance spectroscopy (EIS) studies reveal that Ni incorporation not only decreases the Ohmic resistance (R_s) and charge transfer resistance (R_{ct}), but also enhances the Li^+ diffusion coefficient in the cathode. Moreover, in general, the $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{O}$ electrode demonstrates diffusion coefficient to be

Figure 2 (a, b) Top-view scanning electron microscope (SEM) and the CV activation process of the $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{O}@\text{C}$ electrode. (c) XRD patterns of the $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{O}@\text{C}$ electrode before and after activation. Reprinted with permission from Ref. [55], Copyright 2017, Wiley. (d) SEM image of $\text{NaTi}_2(\text{PO}_4)_3$. (e) Schematic illustration of the interfacial deposition process of $\text{Na}_4\text{Ti}(\text{PO}_4)_2(\text{OH})_2$. (f) XRD of the products prepared in 4 mol L^{-1} $\text{NaTi}_2(\text{PO}_4)_3$ with 1, 2, 3, and 6 h of reaction. Reprinted with permission from Ref. [75], Copyright 2021, Wiley. (g–i) SEM image, CV, *ex situ* FTIR and EELS spectra of the $\text{K}_2\text{Fe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]\cdot 2\text{H}_2\text{O}$ electrode. Reprinted with permission from Ref. [78], Copyright 2017, Wiley.

~2.68 times that of pure MnO electrode. The promoted electron transport and ion diffusion ultimately result in much better rate performance of the $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{O}$ cathode, facilitating its pairing with AC anode. Interestingly, the solid-solution cathode is able to store energy within a wide potential range of 0–1.4 V *versus* saturated calomel electrode enabled by a simple but unique CV activation. After ca. 10 times of CV cycling, the $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{O}$ cathode almost suppresses the oxygen evolution in the high potential range (Fig. 2b). Fig. 2c exhibits the X-ray diffraction (XRD) result, which evidences the novel phase transformation of $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{O}$ before and after the activation from highly crystalline $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{O}$ to poorly crystallized $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, which is believed to dominantly utilize transferred electrons (competing with water). Consequently, the assembled ALIC worked well within a ultrahigh voltage window of 2.4 V, delivering the maximum volumetric energy density of $4.72 \text{ mW h cm}^{-3}$ and power density of 776 mW cm^{-3} . ASICs were also assembled using high-quality $\text{NaTi}_2(\text{PO}_4)_3$ and N-doped carbon. The porous single-crystal $\text{NaTi}_2(\text{PO}_4)_3$ with uniform size was fabricated *via* a novel liquid transformation of ultrathin TiO_2 nanosheets

and subsequently coated with a conductive carbon sheath [66]. $\text{NaTi}_2(\text{PO}_4)_3@\text{C}$ exhibits high capacities of $80\text{--}102 \text{ mA h g}^{-1}$ at varied current densities of $0.5\text{--}3 \text{ A g}^{-1}$, benefitting from the synergistic effect of efficient ion diffusion enabled by the porous network and improved electronic conductivity and structural stability provided by the coated carbon shell. Consequently, the ASICs achieve a high first discharge capacity of 89 mA h g^{-1} at 0.5 A g^{-1} , and the high value of the capacity remains (63 mA h g^{-1}) even after 400 cycles.

$\text{NaTi}_2(\text{PO}_4)_3$ with a nanowire array structure was also specifically designed to enable the construction of high-performance ASICs [75]. $\text{NaTi}_2(\text{PO}_4)_3$ nanowires were grown on thin titanium foil (Fig. 2d) by elaborately utilizing the weak ionization chemistry of NaH_2PO_4 (NHP), where single-agent NHP not only aided in partial etching of titanium to release TiO_2^{2+} , but also induced the interfacial phase transformation of pre-deposited orthomorphous $\text{Na}_4\text{Ti}(\text{PO}_4)_2(\text{OH})_2$ cubes (Fig. 2e) to hexagonal $\text{NaTi}_2(\text{PO}_4)_3$. XRD patterns of the products at different growth stages unambiguously revealed the importance of weak dissociation chemistry of NHP, interfacial deposition, and phase

transformation (Fig. 2f). Benefiting from the hierarchical architecture to facilitate charge and mass transport, the $\text{NaTi}_2(\text{PO}_4)_3$ could stably be operated at significantly high rates of 15–150 C with high capacities. Furthermore, the resulting hydrogel ASIC delivered the maximum volumetric energy density of $\sim 5.8 \text{ mWh cm}^{-3}$ (1.0 mg cm^{-2} $\text{NaTi}_2(\text{PO}_4)_3$). When the $\text{NaTi}_2(\text{PO}_4)_3$ mass loading was increased to 3.5 mg cm^{-2} , the ASIC still achieved high energy density and power density comparable to commercial solid-state thin-film batteries such as Enfilm 700 and Stereax M250.

Compared with the advanced design of Li^+/Na^+ storage electrodes, the design of K^+ storage electrodes for AHSCs is still at the early stage and needs substantial advancement. The driving forces for developing K^+ storage devices are the low cost and abundance (2.09 wt% in the earth's crust) of potassium resources, and the similar physical and chemical properties of K^+ to Li^+ and Na^+ [62]. However, owing to the large-sized K^+ ion ($1.38 \text{ \AA}$) ($r_{\text{Li}^+} = 0.76 \text{ \AA}$, $r_{\text{Na}^+} = 1.02 \text{ \AA}$) and strong K^+-K^+ electrostatic repulsion, the intercalation/insertion of K^+ into crystal lattice of electrode materials is generally more difficult and even it is not easy to stabilize the intercalated/inserted electrode structure. This issue becomes more serious in aqueous electrolytes due to the strong solvation of K^+ by water and the easy dissolution of K^+ -incorporated electrode materials into solution. Consequently, many K^+ storage electrodes exhibit poor cyclability, low capacity, and inferior rate capability in aqueous electrolytes [11]. A strategy to overcome this limitation includes the selection of a new class of electrode materials, for example, PBAs with open-framework structure, which can be easily fabricated by a low-temperature solvothermal process [76,77]. Fig. 2d demonstrates that $\text{K}_2\text{Fe}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6]\cdot 2\text{H}_2\text{O}$ nanocubes with a uniform size distribution can be successfully attained, and they have the perovskite-type structure that can form a 3D channel for fast transport of metal ions without collapse of the crystal framework [78]. As expected, two pairs of well-separated redox peaks are observed at 0.96/0.88 V and 0.34/0.23 V in CV profiles, indicating two-electrons (per formula unit) transfer and exceptionally high capacities. In order to confirm the structural evolution and charge storage mechanism of $\text{K}_2\text{Fe}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6]\cdot 2\text{H}_2\text{O}$ cathode during the electrochemical process, *ex situ* Fourier transform infrared (FTIR) spectroscopy measurements and *ex situ* electron energy loss spectroscopy (EELS) were carried out to record the transformation of the crystal structure (Fig. 2e, f). It was found that the cathode underwent reversible structural evolution upon K^+ intercalation/deintercalation associated with the redox reaction between Fe^{III} and Fe^{II} benefiting from the intrinsic feature of large open-framework structure of K^+ , and the $\text{K}_2\text{Fe}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6]\cdot 2\text{H}_2\text{O}$ cathode demonstrated good rate performance and cycling stability (>500 cycles at 21.4 C). Based on the above mentioned consideration, selection of materials with large open crystal frameworks or channels as the battery-type electrodes of APICs is particularly promising and deserves more in-depth systematic explorations in near future.

Noteworthy, only limited studies on APICs have been carried out till date due to the significant lack in qualified aqueous K^+ storage battery-type materials. Fortunately, techniques applied to aqueous Li^+ and Na^+ electrode materials for improving the rate, cycling, and energy, in principle, can be utilized for K^+ storage as well. With this in mind, several possible categories of battery electrode materials such as titanium- and manganese-based oxides, polyanion-type compounds, and other PBAs can be

envisaged in the near future for developing advanced APICs.

Battery electrodes for alkaline AHSCs

Compared with $\text{Li}^+/\text{Na}^+/\text{K}^+$ intercalation/insertion electrodes in neutral electrolytes, charge storage electrodes in alkaline electrolytes, such as transition metal oxides, hydroxides, and even sulfides, nitrides, and phosphides, in general, offer larger theoretical specific capacity due to their intensive redox activities (when reacting with OH^- , accompanied by the valence changes of transition metal ions) [41,71,73,79–84]. The main drawback is that most of these materials are not well conductive, offering limited electron transport ability. This limitation prevents them from fully engaging in the electrochemical reactions in the alkaline electrolytes, in particular, at high rates. In order to boost the redox reactions within a wide rate range, enhancement in the electronic conductivity while maintaining fast ion diffusion in the solid electrodes is highly desirable. One promising approach involves the design of mesoporous (but continuous) and ordered 3D electrode architecture [34,85,86]. For instance, our group once developed an integrated mesoporous copper-nickel oxide ((Cu,Ni)O) nanowire array, consisting of CuO and NiO uniformly fused into nanowires and offering synergistic effects (Fig. 3a, b) [87]. The interconnected NiO and CuO nanoparticles resulted in the generation of numerous mesopores with a size of $\sim 4 \text{ nm}$, facilitating the electrolyte penetration and shortening the ion diffusion length. Notably, the integration of CuO was found to improve the electronic conductivity of the hybrid electrode. In particular, the molar ratio of Ni to Cu in the nanowires could be readily tuned, thus making the capacity of the electrode highly controllable (Fig. 3c). This helped to optimize the nanowire array cathode and facilitated the flexible charge balance with the AC anode to construct a high-performance device. Consequently, the assembled AHSCs of (Cu,Ni)O₍₊₎/AC₍₋₎ displayed superior rate capability and high power density (5213.4 W kg^{-1}).

Besides architectural design, element doping (with nonmetal, metal, or multi-elements) [84,88,89], coating with conducting carbons or polymers (e.g., polypyrrole (PPy) and polyaniline (PANI)) [44,71], surface functionalization and surface activation [90,91], etc. have also been utilized to improve the electron transport ability and electroactive sites of transition metal compounds electrode. Yang *et al.* [84] demonstrated a good example by fabricating edge site-enriched nickel-cobalt sulfide nanoparticles on graphene (Ni-Co-S/G; Fig. 3d) to form integrated hybrid architectures *via* an *in situ* chemically converted method. The introduction of graphene significantly enhanced the electronic conductivity of the hybrid electrode, and density functional theory (DFT) calculations showed that the Ni-Co-S edges consisted of abundant electroactive sites and strong affinity to OH^- in the electrolyte (Fig. 3e). As a result, an enhanced electrochemical activity was attained, which was further proved by EIS, as shown in Fig. 3f. Benefiting from the strong binding to graphene and the rich redox reaction sites presented at the edges of nanoparticles, an alkaline AHSC device using Ni-Co-S/G hybrids as positive electrode and 2D porous carbon nanosheets (PCNS) as negative electrode delivered a specific capacity of $\sim 122 \text{ F g}^{-1}$ at a high current density of 1 A g^{-1} , which was still 105 F g^{-1} at 10 A g^{-1} with 86% of capacity retention rate.

In recent years, extensive studies have been attempted on alkaline AHSCs using various transition metal oxides/sulfides/phosphides with diverse morphologies as cathode materials. In particular, metal sulfides and phosphides with better con-

Figure 3 (a, b) SEM and transmission electron microscopy (TEM) images of (Cu,Ni)O nanowires. (c) The capacity of nanowires with different Cu:Ni molar ratios. Reprinted with permission from Ref. [87], Copyright 2016, Royal Society of Chemistry. (d–f) TEM images, structural models and EIS of the Ni-Co-S/G hybrids. Reprinted with permission from Ref. [84], Copyright 2016, Royal Society of Chemistry. (g) The anode side shown by the redox/ion-coordination reaction of 1,2-benzoquinone (left) and 1,4-benzoquinone (right) structures. (h) Galvanostatic charge-discharge profiles of PAQS and Ni(OH)₂. (i) Capacity of a Ni(OH)₂/PAQS cell charged/discharged at 25/−25°C. Reprinted with permission from Ref. [99], Copyright 2017, Nature Publishing Group.

ductivity were generally considered than their oxide counterparts [92–94], thus attracting progressively more attention. Nevertheless, continuous charging and discharging in basic electrolyte is likely to result in the formation of transition metal hydroxide as a passivation layer on the electrode surface of metal sulfides and phosphides, which to some extent hinders the subsequent ion diffusion and deteriorates the reaction kinetics [92,95]. As of now, clear and systematic understanding of the fundamentals during this process has not been comprehensively attained. In future research, it is thus quite necessary to explore the underlying charge storage mechanism and principles, and in particular, novel solutions to address the surface evolution issue. Thus, stable, fast-charging, and high-capacity cathodes of metal sulfides and phosphides are highly desirable.

Furthermore, organic materials have also been attracting great interests in aqueous energy storage devices in the past few years [96,97]. One class of such materials is quinones with excellent chemical stability. Their reduction potentials can be readily tuned from 1.7 to 3.2 V *versus* Li⁺/Li upon molecular engineering [98]. In the early period, quinones were mainly considered for nonaqueous metal-ion batteries and aqueous flow

batteries, and their use in other aqueous batteries was quite rare. Despite this, quinones as stable aqueous anode materials have been systematically investigated recently based on a redox/ion-coordination reaction mechanism. For example, 1,2-benzoquinone (left) and 1,4-benzoquinone (right) were reported to store charges efficiently in alkaline/acidic/neutral electrolytes (Fig. 3g) [99]. Poly(anthraquinonyl sulfide) (PAQS) was able to charge and discharge at ~ -0.6 V *versus* standard hydrogen electrode (SHE) with a specific capacity of ~ 200 mA h g^{−1} and low potential polarization (Fig. 3h). The assembled Ni(OH)₂/PAQS device delivered 100% depth of discharge for 1350 cycles at 1 C (200 mA g^{−1}) with 88% capacity retention. It also exhibited excellent rate performance up to 10 C and could work well in a wide temperature range from 25 to −25°C, as displayed in Fig. 3i. The above-mentioned results indicate the great application potential of quinones as anodes in AHSCs.

Transition metal oxides are another type of anode materials for alkaline AHSCs. Among them, iron oxides are promising due to their high theoretical capacity resulting from an aqueous conversion reaction [100,101]. However, the theoretical value can only be realized upon complete conversion ($\text{Fe}^{3+} \rightleftharpoons \text{Fe}^0$)

within a wide negative potential window (extended to ca. -1.3 V vs. Ag/AgCl). As a result, a relatively huge volume change and inevitable water electrolysis (hydrogen evolution) occur during the charge storage process, which eventually leads to drastic decay in capacity and electrode failure after merely tens to a hundred of cycles [102,103]. The rate performance of iron oxide anodes in alkaline electrolyte was also affected by the formation of iron hydroxide passivation layer. To address the above-mentioned problems, our group has made continuous efforts to modify the surface of iron oxides with carbon or oxide layer, for the purpose of restricting the variation in inner volume, which can enhance the electronic conductivity or alleviate hydrogen evolution [104–106]. In detail, a “carbon shell protection” solution and an interesting “carbon glue” penetration strategy (Fig. 4a) toward Fe_3O_4 nanorod film anode [104,105], were, respectively, proposed by our research group. The carbon protection method not only buffered the inner volume expansion of iron oxide and maintained the cycling stability, but also improved the conductivity of anode film, which in combination with the merits of ordered array architecture (i.e., the direct electron transport pathway), enabled good rate capability (Fig. 4b). However, noteworthy, the attractive cycling stability

(after 1000 cycles and 99% capacity retention) could only be obtained at suitable carbonization temperature, as shown in Fig. 4c. Another efficient solution we proposed is the conformal surface coating of amorphous TiO_2 toward iron oxide *via* atomic layer deposition (ALD) [106]. The coating thickness was quite uniform and could be readily tuned by controlling the deposition time. Optimal shell thickness was found to be ~ 10 nm (Fig. 4d) to provide sufficient stabilizing effect, without essential hindering of the ion penetration. In addition to the restricting function, conformal TiO_2 also provided extra capacity *via* Li^+ intercalation/de-intercalation that alleviated the water electrolysis, as illustrated in Fig. 4e. As expected, excellent cycling performance of the $\text{Fe}_3\text{O}_4@/\text{TiO}_2$ electrode up to 30,000 cycles was achieved (Fig. 4f). Nevertheless, the remaining challenge for the ALD-decorated iron oxide anode is that it takes a longer time to be fully activated.

Similar to iron oxides, Bi_2O_3 can also store charges in basic electrolytes *via* multi-electron Faradic processes ($\text{Bi}_2\text{O}_3 + 3\text{H}_2\text{O} + 6\text{e}^- \rightleftharpoons 2\text{Bi}^0 + 6\text{OH}^-$), and due to its low redox potential, it has also been used as the anode material in alkaline batteries and AHSCs. Recent advances have demonstrated that direct growth of arrayed Bi_2O_3 architectures on the current collector (e.g.,

Figure 4 (a–c) SEM images, the features and cycling performance of Fe_3O_4 @carbon glue. Reprinted with permission from Ref. [104], Copyright 2018, Wiley. (d–f) TEM images, structural features and cycling performance of the $\text{Fe}_3\text{O}_4@/\text{TiO}_2$. Reprinted with permission from Ref. [106], Copyright 2018, Wiley. (g, h) SEM and the synthesis route of $\text{r-Bi}_2\text{O}_3/\text{GN/BC}$. (i) Gravimetric capacity of $\text{r-Bi}_2\text{O}_3/\text{GN/BC}$, $\text{Bi}_2\text{O}_3/\text{GN/BC}$, and GN/BC versus different current densities. Reprinted with permission from Ref. [46], Copyright 2017, Wiley.

nanosheet arrays) can lead to the achievement of high capacity and significant enhancement in the rate performance [107,108]. Following this concept, a vertically aligned Bi_2O_3 anode with good crystallinity was further fabricated, which could maintain high-capacity retention of 42.2% when the current density increased 10-fold [109]. Besides arrayed architectures, free-standing electrode can also improve the performance *via* forming a network with mixed ionic/electronic conductivity. For instance, Liu *et al.* [46] reported the fabrication of freestanding oxygen-defective bismuth oxide ($\text{r-Bi}_2\text{O}_3$)/graphene (GN)/bacterial cellulose (BC) electrode with high mass loading (9.8 mg cm^{-2}), which was achieved through a simple solvothermal process and subsequent NaBH_4 reduction (Fig. 4g, h). With strong reductive agent treatment (NaBH_4 solution), $\text{r-Bi}_2\text{O}_3$ /GN/BC acquired abundant oxygen vacancies and endowed Bi_2O_3 with richer active sites and faster charge transfer. As a result, the electrode could achieve 83% of the theoretical value and better rate performance than previously reported Bi_2O_3 electrodes (Fig. 4i). Despite significant progress in recent years, Bi_2O_3 anode is still far from satisfactory for AHSCs owing to its intrinsically poor conductivity and unstable structure arising from volume expansion during prolonged cycling. Doping, surface modification, and advanced structural design processes carried on other battery-type electrodes are believed to be effective for Bi_2O_3 to address these issues.

Battery electrodes for acidic AHSCs

Aqueous batteries using acidic electrolytes such as the state-of-the-art lead-acid batteries have been developed over one and a half century. The technique for lead-acid batteries is quite mature and has been widely used in various fields such as transport vehicles, telecommunications and information technologies. The hybridization of lead-acid battery with SC gives birth to acidic AHSCs, which is a type of AH device defined in our previous review [26]. In recent years, various acidic AHSCs were assembled by using lead dioxide (PbO_2) and carbon materials as the positive electrode and negative electrode, respectively, due to high voltage ($\sim 2 \text{ V}$) of the device and low cost of carbon [110–114]. In general, such acidic AHSCs demonstrated acceptable comprehensive performance and many literatures dealt with the morphological and structural design of PbO_2 cathode and carbon anode. However, long-term cycling was still limited owing to the PbO_2 being sulfated during the charge storage process. The issue of the sulfated PbO_2 could be overcome by using methane sulfonic acid electrolyte instead of sulfuric acid. For example, Perret *et al.* [112] reported the PbO_2 //AC AHSCs that showed 5000 charge/discharge cycles at 22 C rate without any sign of performance degradation in methane sulfonic acid electrolyte. Moreover, increasing the active surface area of PbO_2 electrode is believed to enhance the material utilization and thus increase the capacity of the system [114,115]. For instance, Zhang *et al.* [116] developed a unique 3D-Ti/ PbO_2 positive electrode for acidic AHSCs. The electrode material was synthesized by anodic oxidation on 3D porous conductive substrates, which enabled the *in situ* oxidation of Pb^{2+} to PbO_2 directly on the current collector. Based on the 3D porous Ti substrates with larger surface area and good electrical conductivity, the generated 3D-Ti/ PbO_2 could deliver significantly higher capacity of 132 mA h g^{-1} than Ti- PbO_2 (20.8 mA h g^{-1}). Furthermore, the acidic 3D-Ti/ PbO_2 //AC AHSCs was assembled based on 3D-Ti/ PbO_2 as the positive electrode and AC as the

negative electrode, which displayed good rate performance with an energy density of 30 W h kg^{-1} at a power density of 2078 W kg^{-1} and stable cycling stability with capacitance retention of $\sim 100\%$ after 1000 cycles.

DESIGN OF CAPACITIVE ELECTRODES IN AHSCs

Being opposite to battery-type electrode, capacitive electrode is also crucial to the device performance of AHSCs. Basically, comparable stored charges per electrode area are the prerequisite to achieve reliable matching with battery-type electrode. Recent years have witnessed significant progress in improving the charge storage capability of capacitive electrode in AHSCs. Tuning the pore structure and size of pure EDLC materials (in particular, conductive carbons) to efficiently utilize pores of different size scales (including micropores) has been demonstrated to be an effective method [117]. For pseudocapacitive materials, the most popular way to attain high capacitance is to design elaborated micro-nanostructures capable of providing more active surfaces or interfaces for Faradaic reactions [118]. Other key strategies reported in recent years are: (1) tuning the surface chemistry to enhance electrolyte infiltration and doping EDLC materials to introduce pseudocapacitive contribution; (2) exploration of new-types of EDLC and pseudocapacitive materials (Fig. 1, left side).

Traditional capacitive materials

Carbon-based materials as traditional capacitive materials have been well developed due to the advantages of large specific surface area and good electronic conductivity. The capacitance of carbon materials is attributed to charge accumulation on the material surface *via* physical adsorption to form EDLC. However, the specific surface area of the carbon electrode is theoretically restricted to $2630 \text{ m}^2 \text{ g}^{-1}$ [119], which limits the theoretical capacitance. Moreover, the voltage of device is generally below 2.0 V in aqueous electrolyte. Limited capacitance and device voltage lead to unsatisfactory energy density of AHSCs when carbon-based capacitive electrodes are employed. To address the challenge, some studies have concentrated on heteroatom (N, O, B, S, etc.) doping of carbon materials to increase the capacitance [89,120–122]. The introduction of elemental dopants may enhance the wettability of material surface, increase the electronic conductivity, or induce pseudocapacitance *via* Faradaic reactions of dopants with species in aqueous electrolytes. Consequently, in general, doped carbon electrodes store charges based on a mixed mechanism.

Different from carbon-based capacitive materials, pseudocapacitive materials have relatively high capacitance as a result of the occurrence of dominant redox reactions on the surface or near-surface. Typical materials are RuO_2 [123], MnO_2 [124], V_2O_5 [125], MoS_2 [126], MoO_2 [127], and conducting polymers such as poly(3,4-ethylenedioxythiophene) (PEDOT) [128], PANI [129], and PPy [130]. Among them, metal oxides constitute one promising category that has been widely investigated in recent years; nevertheless, metal oxide materials suffer from poor electronic conductivity and relatively limited cycling stability. Thus, much attention has been paid to boosting the electrochemical performance by coating conducting polymers or carbon-based materials [125,131–133]. The on-purpose designed surface materials not only serve as a conducting agent in the electrodes, but also help to alleviate the structural collapses of the inner metal oxides. A good example was demonstrated by

Qu *et al.* [125], who fabricated a core-shell structure of PPy grown on V_2O_5 nanoribbon using anionic dodecylbenzene-sulfonate (DBS⁻) as a surfactant (Fig. 5a, b). Pyrrole monomer was first adsorbed on the V_2O_5 surface *via* electrostatic interaction between anionic DBS⁻ and protonated pyrrole. Then, the core-shell electrode architecture was attained after adding $FeCl_3$ solution dropwise to ensure the oxidative polymerization of pyrrole. As expected, the structure of PPy@ V_2O_5 electrode exhibited no evident changes during cycling based on the XRD results at different cycling states (Fig. 5c) and this electrode

demonstrated extremely long cycling stability of up to 10,000 cycles. In general, conductive material coating gives similar effect on the electrochemical performance for other metal oxide pseudocapacitive materials. It has been further proven that the combined use of free-standing oxide electrode architecture can maximize the coating benefits and aid in achieving outstanding capacitive charge storage performance [71,86].

Metal carbides/nitrides (MXenes)

To fulfil the demands of developing high-energy AHSCs, new

Figure 5 (a, b) Schematic illustration of PPy growth and coating on V_2O_5 . (c) *Ex situ* XRD of the PPy@ V_2O_5 electrodes. Reprinted with permission from Ref. [125], Copyright 2012, Wiley. (d) Schematic of hybrid structures composed of two types of interleaved nanosheets and intercalated ions or molecules. (e, f) TEM images and CV of 400-KOH- Ti_3C_2 . Reprinted with permission from Ref. [140], Copyright 2017, Wiley. (g) Schematic illustration of the synthetic route of MXene-based hybrid with 2D ordered mesoporous carbon. Reprinted with permission from Ref. [142], Copyright 2017, Nature Publishing Group. (h) CV curves of the $Ti_3C_2T_x$, MnO_2 and $MnO_2/Ti_3C_2T_x$ electrodes. Reprinted with permission from Ref. [145], Copyright 2017, Wiley. (i) Molecular structure of $Ni_3(HITP)_2$. (j) Repeated cycling at 2 A g⁻¹ and Nyquist plot of $Ni_3(HITP)_2$. Reprinted with permission from Ref. [149], Copyright 2017, Nature Publishing Group.

types of pseudocapacitive materials have also been discovered. Among them, transition metal carbides and nitrides (MXenes) have been attracting extensive attention due to their multiple advantages such as metallic conductivity, interlayer structure, and hydrophilic nature of the functionalized surface [134]. MXenes are generally synthesized by selectively etching the A element layers from the ternary carbides and nitrides $M_{n+1}AX_n$ with a general formula of $M_{n+1}X_nT_x$, where M is an early transition metal, X is carbon (C) or nitrogen (N), T represents surface functional groups ($-O$, $-OH$, and $-F$), and $n = 1$ to 3. To certain extent, MXenes may replace carbon-based materials for use in aqueous energy storage devices because of their ultrahigh electronic conductivity of up to $150,000 \text{ S m}^{-1}$ and large specific surface area, which in principle can result in significant value of capacitance of EDLC [135,136]. Besides, various cations (Na^+ , K^+ , NH_4^+ , Mg^{2+} , Sn^{4+}) [137,138], cationic surfactant (cetyltrimethylammonium bromide (CTAB)) [139], and other functional pillared materials [140–142] can be intercalated into MXene layers to stabilize the layered slabs (maintain the high surface area and nanosheet active edges) and tune the interlayer spacing. These ion- or molecule-intercalated MXenes have thus exhibited significantly improved performance *via* an alternative charge storage mechanism termed as “intercalation pseudocapacitance” [143,144]. Moreover, MXene nanosheets can be designed with pores for a large amount of ion accumulation or fast ion diffusion and be assembled with nanosheets of other components to synergistically improve energy storage capability (Fig. 5d) [134].

For instance, a pillared $\text{Ti}_3\text{C}_2\text{T}_x$ MXene (400-KOH- Ti_3C_2) was fabricated *via* cation intercalation and terminal group (OH^-/F^-) removal [140]. The interlayer distance was increased to 1.26 nm (initial Ti_3C_2 : 0.96 nm) after the synthesis, as shown in Fig. 5e. The increase of interlayer spacing in $\text{Ti}_3\text{C}_2\text{T}_x$ facilitated the charge transport and led to the participation of more Ti atoms in redox pseudocapacitive reactions. Therefore, 400-KOH- Ti_3C_2 delivered the highest capacitance of 500 F g^{-1} at the scan rate of 1 mV s^{-1} compared with other samples reported in literature studies (Fig. 5f). As a promising capacitive material, MXene has also been widely utilized to mix with metal oxides (MnO_x , MoO_3 , NiO , etc.) to form MXene-based hybrids. Such hybrid capacitive electrodes can take full advantage of the high conductivity of MXenes and high capacitance of metal oxides. In order to avoid the natural restacking of MXene nanosheets, hybrid layered materials with an alternative component structure can be designed. As a demonstration, layer-by-layer motif architectures were synthesized by introducing F127 (amphiphilic triblock copolymer) spherical micelles and low-molecular-weight phenolic resoles into the interlayer space of MXene nanosheets *via* the hydrogen bonding interaction [142]. Fig. 5g schematically illustrates the synthetic route, exhibiting that 2D ordered mesoporous carbon (OMC) was derived by high-temperature carbonization and further removal of the metal elements *via* chlorination. The finally obtained OMC layers intercalated with the MXene-derived carbon (MDC) layers, which not only prevented restacking, but also facilitated ion diffusion and electron transfer. Consequently, MDC-OMC electrode achieved a high volumetric capacitance of 212 F cm^{-3} at 0.5 A g^{-1} , better than most of the carbon materials reported previously.

With relatively high specific capacitance, MXenes are promising capacitive electrode to couple with battery-type electrode

for constructing AHSCs. Zhu *et al.* [145] reported that the CV curve of $\text{Ti}_3\text{C}_2\text{T}_x$ anode possessed highly capacitive behavior in Na_2SO_4 electrolyte (Fig. 5h). The weak Faradaic peaks observed in the rectangular curve were attributed to the intercalation of Na^+ into the 2D interlayer of MXene, which can be expressed as follows: $\text{Ti}_3\text{C}_2\text{T}_x + y\text{Na}^+ + ye^- \rightarrow \text{Na}_y\text{Ti}_3\text{C}_2\text{T}_x$. Furthermore, an AHSC device using MnO_2 as the positive electrode and $\text{Ti}_3\text{C}_2\text{T}_x$ as the negative electrode was assembled, which demonstrated a capacitive feature with a high voltage of 2.4 V (Fig. 5h). In the device assembly, MnO_2 was applied within a relatively wide potential range as a battery-type electrode (with obvious redox peaks); however, its stored charges did not match well with $\text{Ti}_3\text{C}_2\text{T}_x$ anode, as shown in Fig. 5h (upper). This explains the distorted rectangular CV profile of the full-cell device (Fig. 5h, bottom). Nevertheless, the couple of pseudocapacitive electrode and battery-type electrode is quite promising for potentially improving the energy density of AHSCs [26], and the performance of $\text{MnO}_2//\text{Ti}_3\text{C}_2\text{T}_x$ AHSC can principally be further optimized *via* tuning the mass loading and redox potential window of the two electrodes.

Metal-organic frameworks

Another new class of capacitive materials are metal-organic frameworks (MOFs), which are crystalline porous materials with high surface area exceeding that of AC. MOFs have demonstrated great application potentials in several fields such as catalysis, semiconductors, and adsorbents due to their large surface area, tunable pore size, and diverse structures [146–148]. Featured with controllable pore size and redox sites, some MOFs are also expected to be used in SCs. Unfortunately, MOF materials generally demonstrate inherent poor electronic conductivity that hinders the electron transport efficiency. Synthesis of conducting MOFs is of extreme importance to overcome this limitation. A typical demonstration was the design of $\text{Ni}_3(2,3,6,7,10,11\text{-hexaiminotriphenylene})_2$ ($\text{Ni}_3(\text{HITP})_2$) with high electronic conductivity, which was further utilized to assemble an SC made entirely from neat MOFs as active materials without any conductive additives and binders [149]. Interestingly, the as-grown $\text{Ni}_3(\text{HITP})_2$ was composed of stacked π -conjugated 2D layers with 1D cylindrical channels of $\sim 1.5 \text{ nm}$ diameter (Fig. 5i), showing high electronic conductivity ($\sim 5000 \text{ S m}^{-1}$; exceeding those of ACs and holey graphite) and spacious space to accommodate large electrolyte ions used in EDLCs. At the low discharge rate of 0.05 A g^{-1} , $\text{Ni}_3(\text{HITP})_2$ EDLC displayed a gravimetric capacitance of 111 F g^{-1} , which was comparable to that of the state-of-the-art AC and higher than that of carbon nanotubes (CNTs). Moreover, $\text{Ni}_3(\text{HITP})_2$ -based SCs exhibited a very high surface area-normalized capacitance of $18 \mu\text{F cm}^{-2}$ and very low equivalent series resistance, as well as capacity retention higher than 90% over 10,000 cycles (Fig. 5j).

It is envisaged that conductive MOF-based capacitive electrodes with large specific capacitance are quite promising for potential use in future AHSCs. In addition to contributing EDLC capacitance *via* accumulation of charges in the regular structural pores, it is also possible that MOFs exhibit pseudocapacitive charge storage ability upon ion uptake accompanied with mild Faradaic reactions. Nevertheless, intense redox reaction with ion insertion into pores of MOFs can lead to a battery-type charge storage mechanism [150]. In this case, MOFs may also be utilized to construct AHSCs, but may not serve as a capacitive electrode any more. Storing charges in MOFs based

on bulk redox reactions is likely to destroy the uniform pore structure due to the significant valence change of metal ions for compensating charges; consequently, issues related to their cycling stability emerge. It therefore seems that pristine MOFs are more suitable to be utilized as capacitive (EDLC or pseudocapacitive) electrode materials.

DESIGN OF ELECTROLYTES

Quasi-solid-state (hydrogel) electrolytes

Electrolyte is the key component in AHSCs that provides an ionic pathway between the battery-type electrode and capacitive electrode. In general, liquid electrolyte can provide rapid ion transport due to its low viscosity and good ability to conduct ions. However, the use of liquid electrolytes limits the development of multifunctional and flexible energy storage devices for applications in flexible and miniaturized electronics because of the leakage risk under various mechanical strains and working temperatures [151]. In this case, quasi-solid-state (hydrogel) electrolytes provide promising opportunity to solve the above-stated critical issue, which not only retains the advantage of liquid electrolyte to provide sufficient ionic conductivity and ensures intimate interfacial contact, but also inherits the relatively high mechanical property of solid polymer electrolytes.

Our group once developed a quasi-solid-state ultrathin AHSC device with a total thickness of $\sim 40\ \mu\text{m}$, which consisted of vanadium oxide nanoarray electrodes and gel (polyvinyl alcohol (PVA)) electrolytes (Fig. 6a) [152]. With the utilization of hydrogel electrolytes and nanoarray architecture, the negative electrode and positive electrode were densely integrated to obtain a thin AHSC device. As expected, the device demonstrated good rate capability (Fig. 6b). Moreover, another quasi-solid-state AHSC displayed excellent flexibility [104]. CVs of the device at different bending angles (30° – 180°) were still able to maintain similar profile (Fig. 6c). Fig. 6d shows the EIS results,

exhibiting that Nyquist plots of the device changed a little with shape deformation, indicating that the ion diffusion process was not significantly influenced. The outstanding mechanical endurance of the device stemmed from the full integration of gel electrolyte into a 3D nanoarray electrode, which was believed to buffer the generated stress upon severe bending, avoiding the formation of cracks that would happen in the case of dense films with liquid electrolyte. The AHSC device further endured high pressures of up to $\sim 32.9\ \text{kPa}$ and worked well within a wide temperature window of 20 – 80°C (Fig. 6e, f) [105]. These multifunctionalities can be ascribed to the intrinsic merits of gel electrolytes compared with those of conventional liquid electrolytes.

Hydrogel electrolytes consist of salts, polymer, and some amount of water. In principle, the ionic conductivity of hydrogel electrolyte is determined not only by the remaining water, but also by the polymer. Different polymers have different water accommodation abilities and show distinct coordination interactions with metal carrier ions, thus exerting strong influence on the ionic conductivity. The interaction between the polymer and water also significantly impacts the functionality and environmental suitability of electrolytes. In addition to PVA, other polymers such as polyethylene glycol, gelatin, sodium carboxymethylcellulose (CMC), polyacrylamide (PAM), and sodium polyacrylate (PANa) have been extensively investigated for aqueous energy storage in recent years [151]. As an example, a new gel electrolyte utilizing PANa as superabsorbent polymer endowed a Zn^{2+} storage device with a high ionic conductivity and water-retaining capability [153]. This superabsorbent polymer consists of a 3D crosslinked network, in which hydrophilic groups and organic groups of the carbon chains exhibit the ability of adsorbing and retaining substantial water molecules. In another study, Zhu *et al.* [154] reported an anti-freezing polyacrylamide hydrogel (PAAm) consisting of cooperative cations ($2\ \text{mol L}^{-1}\ \text{ZnSO}_4$ and $4\ \text{mol L}^{-1}\ \text{LiCl}$). The $\text{Zn}^{2+}/\text{Li}^+$ mixture

Figure 6 (a) SEM image of the PVA electrolyte. (b) Areal capacitance of the solid-state device. Reprinted with permission from Ref. [152], Copyright 2017, Royal Society of Chemistry. (c) Charge-discharge curves and (d) EIS data at different bending/twisting states of 1–4. Reprinted with permission from Ref. [104], Copyright 2018, Wiley. (e, f) Stored charge variation and CVs at different temperatures and pressures. Reprinted with permission from Ref. [105], Copyright 2015, Wiley.

cations cooperatively dissociated the intermolecular hydrogen bonding between water molecules by the cooperative hydration, which significantly reduced the freezing temperature of the hydrogel. Consequently, the device could retain 98% capacity retention upon cooling down to -20°C and showed near 100% capacity retention with >99.5% Coulombic efficiency over 500 cycles at -20°C .

High-voltage electrolytes

Despite the fact that asymmetric device configuration has pushed the voltage window of AHSCs beyond the thermodynamic stability window of water (1.23 V), the experimentally achieved voltage of AHSCs is still limited (< 2.5 V). This brings a significant challenge on the energy output enhancement. An effective approach proposed in recent years to increase the energy density is the use of “water-in-salt” electrolyte (WISE),

which has been mostly applied for various battery devices [155,156]. WISEs were first explored by dissolving lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) in water, at extremely high concentrations (molality > 20 m, molality (m) = mole of solute/weight of solvent (mol kg^{-1})) [157]. Interestingly, with this super-concentrated electrolyte, a dense solid electrolyte interphase (SEI with Li_2CO_3 and LiF-based components; conducting ions but insulating electrons) was formed on the surface of anode. Moreover, anion-containing Li^+ solvation sheath also emerged to reduce the water activity, synergistically expanding the electrochemical stability window of the aqueous electrolyte to ~ 3.0 V (Fig. 7a–c) [158]. This breakthrough motivated researchers to systematically explore more types of WISEs and utilize them in AHSCs. Consequently, a Na^+ AHSC using superconcentrated sodium perchlorate (NaClO_4) as the aqueous electrolyte was reported [159]. The NaClO_4 electrolyte with a

Figure 7 (a) SEI formation mechanisms in WISE. Reprinted with permission from Ref. [158], Copyright 2017, American Chemical Society. (b) Illustration of the evolution of the Li^+ primary solvation sheath in diluted and WIS solutions. (c) The electrochemical stability window of the $\text{LiTFSI}/\text{H}_2\text{O}$ electrolytes. Reprinted with permission from Ref. [157], Copyright 2015, American Association for the Advancement of Science. (d) The electrochemical stability windows of the WISIL [$\text{LiTFSI}/\text{H}_2\text{O}/(\text{EMIM-TFSI})_{2.0}$]. Reprinted with permission from Ref. [161], Copyright 2020, Elsevier. (e) Electrochemical stability window of the full cell with HANE. Reprinted with permission from Ref. [162], Copyright 2018, Elsevier. (f) Potential window of $\text{Li}(\text{TFSI})_{0.7}(\text{BETI})_{0.3} \cdot 2\text{H}_2\text{O}$ compared with that of a typical $1.2 \text{ m LiTFSI}/\text{H}_2\text{O}$ solution with $\text{Li}_4\text{Ti}_5\text{O}_{12}$, LiCoO_2 and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes. Reprinted with permission from Ref. [163], Copyright 2016, Nature Publishing Group.

high concentration of 17 m could enlarge the practical stability window to ~2.75 V. It was reported that all water molecules were incorporated into Na^+ hydration shells *via* the coordination of the Lewis-basic oxygen atoms with Lewis-acidic Na^+ , significantly reducing their activity. Moreover, Na_2CO_3 can be detected on the anode surface functioning as an *in situ* generated SEI to prevent water from transferring electrons with anode, further helping to inhibit water electrolysis [160]. In order to further decrease the water content in the WISEs, “WIS/ionic liquid” electrolyte (WISILE) was developed for ALICs [161]. Less water, LiTFSI, and 1-ethyl-3-methylimidazolium FSI (EMIM-FSI) with a molar ratio of 1:1:2 were utilized. The EMIM-FSI salt can act as a co-solvent to dissolve LiTFSI, thus reducing the water content in the system. Furthermore, the use of the larger sized EMIM⁺ ions with high concentration decreased the distribution of water molecules near the electrode surface, making the decomposition of water molecules more difficult. As expected, the WISILE with inherently moisture-tolerant property could expand the electrochemical stability window of the device to 3.8 V as presented in Fig. 7d, indicating a ~1.0 V extension compared with that (~2.8 V) of the 21 m WISE.

Noteworthy, the formation of anion-originated SEI is not feasible due to the repulsion of anions by negatively polarized anode surfaces. Therefore, Wang *et al.* [162] designed a hybrid aqueous/non-aqueous electrolyte (HANE) that could *in situ* generate hybrid interphase (anion/solvent-originated SEI). HANE combined aqueous solvents (LiTFSI; ~14 mol L⁻¹) with non-aqueous solvents (dimethyl carbonate (DMC)). This type of hybrid electrolyte could inherit the non-flammability and non-toxicity characteristics from the aqueous system and high electrochemical stability from the non-aqueous system. Moreover, non-aqueous portion (solvent) introduced a secondary ingredient (alkylcarbonate) to the protective interphase on the electrode in addition to the LiF from anion reduction. During the charging/discharging process, the unusual interphasial structure in HANE was constructed to more effectively block the electron tunnel, while leading to better conduction of Li⁺ across it. Therefore, HANE could even expand the electrochemical window to 4.1 V, as shown in Fig. 7e.

Another hydrate-melt electrolyte using Li salt hydrate melt can also extend the stability window of aqueous electrolytes to ~3.1 V [163]. Room-temperature hydrate melts of two specific Li salts were evaluated to explore their optimized eutectic systems with the objective of expanding the voltage range at ambient temperatures. Based on the potential windows evaluated for various metal electrodes by linear sweep voltammetry at a low scan rate (0.1 mV s⁻¹) (Fig. 7f), the Li(TFSI)_{0.7}(BETI)_{0.3}·2H₂O hydrate melt provided a wide potential window of 3.1 V. Hydrate-melt electrolytes are essentially WISEs, considering the mass ratio of salts to water used. Moreover, strong interactions also occur between the salts and limited water, and the interfacial SEI is also formed on the electrode surface during the charge storage process, thus reducing the water activity in the way similar to that in the aforementioned LiTFSI WISEs.

In general, WISEs are too expensive to support the sustainable development of AHSCs, in particular, when using lithium salts. In recent five years, the concept of concentrated electrolytes has been successfully extended to other types of aqueous EESs, such as Na⁺, K⁺, and Zn²⁺-based energy storage devices [155,156]. Despite considerable progress, huge challenges still remain

because of the presence of few salts with extremely high solubility in water, high suitability for SEI chemistry (fluorine-containing salt), and high chemical and electrochemical stability in aqueous environments. The recently developed new class of inert cation-assisted WISE (IC-WISE) has shown great promise to provide more opportunities for relieving the above-stated dilemma. Jiang *et al.* [164] reported the construction of tetraethylammonium (TEA⁺)-assisted WISE to improve the solubility of Na⁺ WISE, showing the highest total salt concentration of 31 mol kg⁻¹ (9 m NaOTF + 22 m inert TEAOTF), corresponding to the highest salt/water weight ratio of 7.69. This was attributed to the fact that highly concentrated mixed NaOTF and TEAOTF solutions could generate new ionic structures such as contact ion pairs (CIP = 32%) and aggregate pairs (AGG = 13%). As expected, the Na⁺ IC-WISE could expand the electrochemical window to 3.3 V, with the suppression of transition metal dissolution from the battery-type electrode during cycling. Moreover, using super sucrose electrolyte and molecular crowding electrolyte without the high-concentration salt can also expand the electrochemical stability window of aqueous devices by reducing the amount of free water and destroying the tetrahedral structure (the hydrogen bonds) of free water molecules [49].

So far, high-voltage electrolyte-based AHSCs are still at the infant stage. Several examples reported on using high-concentration electrolytes for AHSCs include 40.4 m CH₃COOK and 9.8 m CH₃COOLi for ALICs [165], 17 m NaClO₄ for ASICs [160], and 1 m Zn(CF₃SO₃)₂ for Zn²⁺ AHSCs [2]. For example, Deng *et al.* [165] reported a low-cost LiMn₂O₄//AC ALIC with a Li⁺/K⁺ mixed superconcentrated aqueous electrolyte (40.4 m CH₃COOK and 9.8 m CH₃COOLi). Fig. 8a demonstrates that in this electrolyte, one Li⁺ and K⁺ hydration separately required four and five water molecules, and the acetate ions associated water molecules were connected *via* hydrogen bond. The molar ratio value between water molecules and total cations was determined to be 1.3:1, and thus there existed hardly any free water molecules in the superconcentrated electrolyte. As a result, the limited bonded water was difficult to be oxidized or reduced, resulting in 2.85 V electrochemical stability window (Fig. 8b). Benefiting from the superconcentrated electrolyte, the as-designed ALIC was also able to be operated in a wider temperature range compared with that using the conventional low-concentration electrolyte (Fig. 8c, d). At 60°C, an energy density as high as 77.9 Wh kg⁻¹ was achieved at the power density of 149.1 W kg⁻¹. Another ALIC using WISILE was assembled with Nb₂O₅ and AC as the anode and cathode, respectively, which exhibited ultrastable higher-voltage window of 2.8 V (Fig. 8e, f) [161]. The charge-discharge curves at different current densities were slightly deviated from the linear profile of an ideal capacitive behavior, a characteristic of a hybrid device. Fig. 8g illustrates that the AC//Nb₂O₅ ALIC still delivered a high energy density of 16.4 Wh kg⁻¹ at the power density of as high as 4.9 kW kg⁻¹. The ALIC further exhibited long-term stability for up to 3000 cycles at 1.0 A g⁻¹ with nearly 100% Coulombic efficiency (Fig. 8h).

With the high voltage window enabled by such electrolytes, AHSCs are expected to demonstrate the highest energy density among various types of AHSCs, considering their high capacitance as well. Nevertheless, SCs should also deliver high power density to differentiate them from batteries, and fast ion transport in electrolytes and efficient charge transfer at the electrode/

Figure 8 (a, b) Schematic illustration of the cation solvation and electrochemical stability window of the high- and low-concentration electrolytes. (c, d) Specific discharge capacities and the energy density of the ALICs in both the electrolytes at different temperatures. Reprinted with permission from Ref. [165], Copyright 2019, Elsevier. (e–h) Electrochemical performance of the AC//Nb₂O₅ ALIC device. The numbers in brackets refer to the cited references in Ref. [161]. Reprinted with permission from Ref. [161], Copyright 2020, Elsevier.

electrolyte interface must be ensured. In this regard, special attention should be paid in future to increasing the ionic conductivity of high-voltage aqueous electrolytes, without drastically increasing the viscosity and avoiding the inevitable salt precipitation at low temperatures [49].

NEW CONFIGURATIONS OF AHSCs

To optimize the electrochemical performance and promote the application potentials of AHSCs, the design of novel device configuration is also of great importance. Till date, new types of AHSCs have rarely been investigated. Nevertheless, there are already related interesting examples reported in literatures. For example, our group constructed a novel all-oxide AHSC using conductive MoO₂-C as the capacitive negative electrode and NiCo₂O₄ as the battery-type positive electrode in aqueous LiOH electrolyte, showing a unique “dual-ion insertion” energy storage mechanism and good electrochemical performance [166]. Different from the charge storage process in conventional AHSCs, the anode and cathode of NiCo₂O₄//MoO₂-C AHSC reversibly intercalate cations (Li⁺) and anions (OH⁻), respectively, as illustrated in Fig. 9a. In most alkaline AHSCs using Ni and Co-based cathodes, the coupling anodes are EDLC carbon materials. Herein, instead, the capacitive MoO₂-C was used, which stored charges *via* surface/near-surface Li⁺ insertion into MoO₂ and

thus provided significant pseudocapacitance. Noteworthy, in basic electrolytes, it is difficult to find suitable pseudocapacitive oxide storing charges using OH⁻ (usually battery-type redox reaction), and thus dual-ion utilization has played a critical role in this configuration. As expected, the AHSC device demonstrated quasi-linear charge-discharge profiles (Fig. 9b) and delivered a high energy density and power density (41.8 W h kg⁻¹ and 19,922.2 W kg⁻¹) (Fig. 9c) compared with AC anode-based alkaline AHSCs.

Another unconventional AHSC is non-polarity structurally symmetric AHSC that can principally be charged in arbitrary direction without specific engineering protection. In 2017, a non-polarity full cell was assembled using conductive vanadium trioxide@carbon (V₂O₅@C) nanosheet arrays as both the anode and cathode [152]. The energy storage mechanisms involved the redox reactions of vanadium ions upon Li⁺ uptake, corresponding to redox couples of V³⁺/V²⁺ and V⁴⁺/V³⁺ for the anode and cathode, respectively (Fig. 9d). Furthermore, CV profiles shown in Fig. 9e indicate that the redox reaction in the anode dominantly represented battery behavior, while that in the cathode featured pseudocapacitive character. Despite the use of the same material as both electrodes, the charge storage mechanisms are quite different, making the full cell operate like AHSCs. On the other hand, exactly due to the symmetric device

Figure 9 (a) Schematic illustration of the configuration and working mechanism of the AHSC device. (b, c) The charge-discharge curves and Ragone plot of the AHSC device. Reprinted with permission from Ref. [166], Copyright 2016, American Chemical Society. (d) Schematic illustration of the 2.0 V V₂O₅@C//V₂O₅@C device. (e) CVs of the V₂O₅@C electrode. (f) Stored charge of the V₂O₅@C with different glucose concentrations. Reprinted with permission from Ref. [152], Copyright 2017, Royal Society of Chemistry. (g) Schematic illustration of the charge storage mechanism of the AHSC device. (h, i) Cycling stability and lighting LED indicator, demonstrating the non-polarity feature. Reprinted with permission from Ref. [167], Copyright 2018, Elsevier.

structure, this type of AHSC has no polarity and it is not necessary to point out which side is positive or negative electrode when the cell is fully discharged and ready for next-round charging. The use of the same anode and cathode material to construct AHSCs further brings benefit for acquiring charge balance. Fig. 9f exhibits that with different carbon coating amounts (*via* changing glucose concentration), the V₂O₅@C anode and cathode always exhibit comparable charge storage ability. Benefiting from the “carbon-protection” effect and the use of PVA-LiCl gel electrolyte, significant alleviation in the vanadium dissolution and structural damage was observed; thus, the charge balance between the two electrodes could be maintained during long-term cycling. Consequently, the device was quite stable and could remain ~93% of the initial capacitance value upon 6000 cycles at a high current density of 2 mA cm⁻². Later, non-polarity AHSCs were further developed by using the binder-free nickel nanoparticle@carbon nanotube (Ni@CNT) as both the negative and positive electrodes (Fig. 9g) [167]. This device could readily operate in basic electrolyte with the efficient utilization of the Faradaic redox reactions of Ni²⁺/Ni³⁺ at the

positive side and EDLC charge accumulation on CNTs at the negative side. It exhibited good electrochemical stability without capacitance loss after 10,000 cycles with alternative change of the charging direction, indicative of excellent non-polarity feature (Fig. 9h). Moreover, the device could power a 5-mm-diameter round red light-emitting diode indicator (LED; 1.8 V, 20 mA) after getting charged in two different directions (Fig. 9i).

Compared with the above AHSCs employing monovalent ions, AHSCs with multivalent-ion storage (Zn²⁺, Mg²⁺, Ca²⁺, Al³⁺) are also under design and development due to the theoretically high energy density resulting from the multielectron redox reaction involved in the battery-type electrode side [35,36,168–170]. Among them, Zn²⁺ AHSCs using Zn as the anode and capacitive materials as the cathode have been attracting significant research attention because Zn has a high volumetric capacity of 5855 mA h cm⁻³, suitable redox potential (−0.763 V *versus* SHE), and good electrochemical reversibility in aqueous electrolytes [171]. Unfortunately, the development of Zn²⁺ AHSCs has been hindered by several factors. For the battery-type electrode, the dendrite growth still exists during plating

and stripping, leading to safety issues and cycling instability of Zn^{2+} AHSCs. Moreover, the sluggish Zn^{2+} diffusion kinetics of Zn anode cannot match well with the rapid ion adsorption/desorption on the capacitive electrode, which limits the power density of Zn^{2+} AHSCs. To solve these issues, many studies focused on using the additives in electrolytes, adjusting the concentration of electrolytes, and designing sophisticated structure of composite anodes [172,173], as presented in Fig. 10. For instance, Wang *et al.* [173] designed the microporous Zn-based MOF (ZIF)-derived anode (annealed at 500°C), in which the trace amount of Zn^0 provided nuclei for further Zn plating to achieve the dendrite-free deposition. The resulting Zn^{2+} AHSCs (AC//ZIF) exhibited ultralong cycling life and dendrite-free behavior for over 20,000 cycles. More recently, an effective strategy to accelerate the kinetics of Zn^{2+} transference and deposition was developed, in which the Zn anode was modified with a 3D nanoporous ZnO architecture [174]. Benefiting from the novel structure, the Zn plating kinetics was accelerated via the electrostatic attraction toward Zn^{2+} rather than the tightly and strongly hydrated one in the electrical double layer, and the H_2 evolution was effectively prevented. Consequently, it achieved an average Zn utilization of 99.55%. For the capacitive electrode, the capacity discrepancy with the battery-type electrode is the key challenge when assembling Zn^{2+} AHSCs. Therefore, considerable efforts have been devoted to introducing heteroatoms or functional groups into the materials, which are expected to provide pseudocapacitive contribution to promote the charge storage capability [175–178]. Furthermore, adjusting the desolvation degree of the solvated Zn ionic clusters can remarkably improve the capacitance of porous carbon materials. The smaller $[\text{ZnCl}]^+(\text{H}_2\text{O})_{n-1}$ clusters were demonstrated to be easier to access micropores in carbon electrodes [179]. Based on this mechanism, porous carbon//Zn AHSCs coupled with ZnCl_2 WISE electrolyte delivered a high energy density of up to 217 Wh kg^{-1} at a power density of 450 W kg^{-1} and an unprecedented cycling life of 100,000 cycles. As multivalent-ion AHSCs have only been defined in recent years, EDLC carbon materials have been mainly utilized as cathode, whereas pseudocapacitive materials have rarely been involved. In this regard, pseudocapacitive cathodes for multivalent-ion AHSCs are expected to be very promising in future studies (Fig. 10). A good recent demonstration used TiN as the pseudocapacitive cathode for Zn^{2+} AHSCs [42]. The effects of various anions (SO_4^{2-} , CH_3COO^- , and Cl^-) in the electrolyte on TiN were carefully investigated by using DFT calculation. It was revealed that SO_4^{2-} anions exhibited the lowest adsorption energy and could easily form the stable structure of TiN- SO_4 after the adsorption process, thus enabling the participation of SO_4^{2-} in the electrochemical process and promoting a two-step adsorption and intercalation energy storage mechanism. Owing to the outstanding electronic conductivity of TiN and the introduction of SO_4^{2-} anions into the electrochemical process, the assembled 1.9 V TiN//Zn AHSC exhibited a quite high capacitance of 489.8 F g^{-1} at a current density of 0.2 A g^{-1} and a capacitance of 314.5 F g^{-1} at a high current density of 1 A g^{-1} after 10,000 cycles. For electrolyte, rational design of the components and structure can further improve the electrochemical performance of Zn^{2+} AHSCs, such as stability and voltage window (Fig. 10). For example, using WISE containing 21 m LiTFSI and 1 m $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ as electrolyte could not only broaden the operating voltage of Zn^{2+} AHSC to 2.2 V, but also enable high capacitance of

Figure 10 Summary of general shortages of Zn^{2+} AHSCs based on Zn anode and the corresponding solutions.

214.3 F g^{-1} after 5,000 cycles [180]. Therefore, to completely avoid the dendrite issue at the anode side, constructing multivalent-ion AHSCs based on capacitive anode and ion-insertion/intercalation battery-type cathode will also be quite interesting [181–183].

CONCLUSION AND OUTLOOK

AHSCs represent an important future direction for the next-generation electrical energy storage, which are expected to provide higher energy density than aqueous SCs and higher power density than aqueous batteries. In this review, recent advances in the optimization of the battery-type electrodes, the capacitive electrodes, and the electrolytes of AHSCs are summarized (Table 1). The ingenious design of some emerging AHSC devices with unique configurations and charge storage process are also presented. Despite the significant progress made in this field, it remains a huge challenge to attain high comprehensive performance of AHSCs for practical applications. Therefore, approaches to simultaneously achieve high energy density, high power density, as well as long cycling stability of AHSCs still need to be investigated. The underlying reasons for the restriction of current device performance are strongly related to the relatively sluggish kinetics and larger structural variation of battery-type electrode and the capacitance limitation of the capacitive electrode, which result in the mismatch of the two electrodes in kinetics and charge storage ability. Noteworthy, substantial improvements in energy and power densities are the prerequisite for improving the competitiveness of AHSCs compared with other aqueous energy storage devices. To address these challenges, more efforts should be devoted to the following aspects.

(1) For the battery-type electrode, the development of unique 3D electrodes is still required. It is well-known that 3D electrodes can principally provide sufficient ion diffusion channels and continuous electron transport pathways, which are ideal electrode architectures to ensure simultaneous ion/electron transportation for synergistically boosting the rate capability of battery-type electrode. Moreover, 3D structure also makes the conformal modification of the electrode with other materials much easier, which is crucial to substantially improve the electrode cycling stability. However, the mass loading of current 3D battery electrodes in AHSCs is still very low. For practical

Table 1 Summary of the electrochemical performance of typical AHSCs

Device/electrode	Electrolyte	Performance	Energy density _{max}	Power density _{max}	Voltage	Ref.
Design of battery-type electrode						
Ni _{0.25} Mn _{0.75} O@C//AC	Aqueous PVA-LiCl	95.5%, 5200 cycles, 12 mA cm ⁻²	4.72 mW h cm ⁻³	776 mW cm ⁻³	0–2.4 V	[55]
Na ₄ Mn ₉ O ₁₈ //AC	Aqueous Na ₂ SO ₄	~100%, 1000 cycles, 4 C	–	–	0.4–1.8 V	[56]
K _{0.45} MnO ₂ -0.3H ₂ O//AC	Aqueous K ₂ SO ₄	–	43.1 W h kg ⁻¹	2500 W kg ⁻¹	0–1.65 V	[58]
K ₂ Fe ^{II} [Fe ^{II} (CN) ₆]2H ₂ O	Aqueous K ₂ SO ₄	>85%, 500 cycles, 21.4 C	–	–	0–1.2 V	[78]
Porous carbon//NaTi ₂ (PO ₄) ₃ @C	Aqueous Na ₂ SO ₄	70%, 400 cycles, 0.5 A g ⁻¹	–	–	0.4–1.6 V	[66]
AC//NaTi ₂ (PO ₄) ₃	PVA-NaClO ₄	79.2%, 10,000 cycles	5.8 mW h cm ⁻³	999 mW cm ⁻³	0–2.4 V	[75]
AC//Bi ₂ O ₃ @C	Aqueous Na ₂ SO ₄ -NaCl	72.3%, 650 cycles, 2 A g ⁻¹	18.94 W h kg ⁻¹	1267 W kg ⁻¹	0–1.9 V	[107]
ZnNiCo-P//reduced graphene oxides	Aqueous KOH	89%, 8000 cycles, 10 A g ⁻¹	60.1 W h kg ⁻¹	19.54 kW kg ⁻¹	0–1.6 V	[39]
KNiPO ₄ //AC	Aqueous KOH	93%, 2000 cycles, 1 mA cm ⁻²	13 W h kg ⁻¹	900 W kg ⁻¹	0–1.5 V	[41]
NiCo ₂ S ₄ @N-doped CNT//AC	Aqueous KOH	88.9%, 3000 cycles, 10 A g ⁻¹	49.75 W h kg ⁻¹	13.4 kW kg ⁻¹	0–1.5 V	[45]
Co ₃ O ₄ /GN/BC//r-Bi ₂ O ₃ /GN/BC	Aqueous KOH	90%, 1000 cycles, 20 mA cm ⁻²	0.449 mW h cm ⁻²	40 mW cm ⁻²	0–1.6 V	[46]
3D CoO@PPy//AC	Aqueous NaOH	91.5%, 20,000 cycles, 25 mA cm ⁻²	43.5 W h kg ⁻¹	5500 W kg ⁻¹	0–1.8 V	[71]
(NH ₄)(Ni,Co)PO ₄ -0.67H ₂ O//porous carbon	Aqueous KOH	77.5%, 7000 cycles, 1 A g ⁻¹	44.5 W h kg ⁻¹	7.4 kW kg ⁻¹	0–1.55 V	[73]
(Cu, Ni)O//AC	Aqueous NaOH	100.9%, 6000 cycles, 5 mA cm ⁻²	50.3 W h kg ⁻¹	5213.4 W kg ⁻¹	0–1.8 V	[87]
Ni-Co-S/G//PCNS	Aqueous KOH	85%, 10,000 cycles, 10 A g ⁻¹	43.3 W h kg ⁻¹	22.1 kW kg ⁻¹	0–1.6 V	[84]
Cabon/PbO ₂ //AC	CH ₃ SO ₃ H+Pb(NO ₃) ₂ +NaNO ₃	100%, 5000 cycles, 10 mA cm ⁻²	29 W h kg ⁻¹	–	0–2.1 V	[112]
SiO ₂ /PbO ₂ //AC	Aqueous H ₂ SO ₄	91%, 1000 cycles, 3 A g ⁻¹	61 W h kg ⁻¹	–	0–2.4 V	[115]
3d-Ti/PbO ₂ //AC	Aqueous H ₂ SO ₄	99.2%, 1000 cycles, 5 mA cm ⁻²	49.4 W h kg ⁻¹	–	0–2.3 V	[116]
Design of capacitive electrode						
n-Ti ₂ CT ₂ /C//Zn	LiTFSI+Zn(CF ₃ SO ₃) ₂ WIS	96%, 12,500 cycles, 0.5 A g ⁻¹	–	–	0–2 V	[43]
NiO/rGO//PANi12.5	Aqueous KOH	~100%, 100,000 cycles, 5 A g ⁻¹	81 W h kg ⁻¹	13,794 W kg ⁻¹	0–1.6 V	[44]
V ₂ O ₅ @C//Fe ₃ O ₄ @TiO ₂	PVA-LiCl	–	2.23 mW h cm ⁻³	1090 mW cm ⁻³	0–2 V	[106]
PPy@V ₂ O ₅ //AC	Aqueous K ₂ SO ₄	95%, 10,000 cycles, 10 C	42 W h kg ⁻¹	2.5 kW kg ⁻¹	0–1.8 V	[125]
NiCo ₂ O ₄ /MnO ₂ //MoO ₃ /PPy	Aqueous Na ₂ SO ₄	88.2%, 10,000 cycles, 4 mA cm ⁻²	60.4 W h kg ⁻¹	2400 W kg ⁻¹	0–1.6 V	[130]
Cobalt-aluminum layered double hydroxide/Ti ₃ C ₂ T _x	Aqueous KOH	90%, 5000 cycles, 4 A g ⁻¹	–	–	0–0.6 V	[141]
MDC-OMC	Aqueous KOH	98%, 7000 cycles, 4 A g ⁻¹	–	–	–1–0 V	[142]
MnO ₂ //Ti ₃ C ₂ T _x	Aqueous Na ₂ SO ₄	95.9%, 450 cycles, 100 mA g ⁻¹	113 W h kg ⁻¹	6000 W kg ⁻¹	0–2.4 V	[145]
Design of electrolytes						
Zn//AC	Water/ethyleneglycol-ZnSO ₄	80%, 5000 cycles, 10 A g ⁻¹	56.44 W h kg ⁻¹	8153 W kg ⁻¹	0–1.6 V	[36]
CNTs//Fe ₃ O ₄ -C	PVA-KOH	67.7%, 1000 cycles, 5.5 mA cm ⁻²	1.56 mW h cm ⁻³	0.48 W cm ⁻³	0–1.6 V	[105]
PCMS//PNTCDA	NaClO ₄ WIS	86%, 1000 cycles, 1 A g ⁻¹	65.1 W h kg ⁻¹	20 kW kg ⁻¹	0–2 V	[159]
AC//Nb ₂ O ₅	LiTFSI/(EMIM-TFSI) _{2.0} WIS	84%, 3000 cycles, 1 A g ⁻¹	51.9 W h kg ⁻¹	4.9 kW kg ⁻¹	0.8–2.8 V	[161]
LiMn ₂ O ₄ //AC	CH ₃ COOLi/K WIS	100%, 20,000 cycles, 10 A g ⁻¹	58 W h kg ⁻¹	6000 W kg ⁻¹	0–2 V	[165]
The advanced new-type AHSCs						
AC//Zn	Zn(CF ₃ SO ₃) ₂ -acetonitrile	91%, 20,000 cycles, 1 A g ⁻¹	52.7 W h kg ⁻¹	–	0–1.8 V	[2]
TiN//Zn	PAM-ZnSO ₄	~84%, 3500 cycles, 0.5 A g ⁻¹	–	–	0.1–1.9 V	[42]
V ₂ O ₅ @C//V ₂ O ₃ @C	PVA-LiCl	93%, 6000 cycles, 2 mA cm ⁻²	15.9 mW h cm ⁻³	6800 mW cm ⁻³	0–2 V	[152]
NiCo ₂ O ₄ //MoO ₃ -C	Aqueous LiOH	130%, 3000 cycles, 10 mA cm ⁻²	41.8 W h kg ⁻¹	19.922 kW kg ⁻¹	0–1.8 V	[166]
Ni@CNT//Ni@CNT	PVA-KOH	100%, 10,000 cycles, 50 mA cm ⁻²	1.39 mW h cm ⁻³	440 mW cm ⁻³	0–1.8 V	[167]
MnO ₂ //AC	Aqueous Zn(CF ₃ SO ₃) ₂	93.4%, 5000 cycles, –	29.5 W h kg ⁻¹	–	0–2 V	[169]
AC//ZIF	Aqueous ZnSO ₄	72%, 20,000 cycles, 4 A g ⁻¹	140.8 W h kg ⁻¹	2850 W kg ⁻¹	0.2–1.8 V	[173]
Porous carbon//Zn	ZnCl ₂ WIS	95.1%, 100,000 cycles, 5 A g ⁻¹	217 W h kg ⁻¹ (based on carbon materials)	–	0–1.8 V	[179]
Phosphorene//Zn	ZnCl ₂ -Et ₄ NBF ₄ /PC	33%, 90,000 cycles, 0.5 A g ⁻¹	315.6 W h kg ⁻¹ (based on the phosphorene)	23,582.4 W kg ⁻¹	0–2.5 V	[180]
AC//Zn	Aqueous ZnSO ₄	91%, 10,000 cycles, 1 A g ⁻¹	84 W h kg ⁻¹	14.9 kW kg ⁻¹	0.2–1.8 V	[183]

application, it is very important to discover novel synthesis or processing methods to increase the mass loading while maintaining the benefits of 3D architecture.

(2) For capacitive electrode, the future material selection and micro-nanostructure design should further focus on new pseudocapacitive materials, in particular, high-conductivity MOFs, conductive 2D MXenes, and “intercalation pseudocapacitive oxides” such as MoO_x , Nb_2O_5 . These promising materials can exhibit higher capacitance than traditional EDLC materials, in particular, when normalized to volume. It is therefore more convenient to achieve the charge balance with the battery-type electrode when assembling AHSCs devices. In order to design multivalent ion AHSCs using pseudocapacitive materials, it is necessary to systematically investigate the charge storage process and kinetics of these materials upon multivalent ion insertion. Theoretical calculation, computing modeling, and *in situ* or *ex situ* probing of the evolution of the crystal/electronic structure, phase, and micro-nanostructure are of extreme significance to unveil the charge storage mechanism and distinguish it from diffusion-controlled Faradaic reactions.

(3) Electrolyte is another key parameter in AHSCs, which is not only strongly related to the energy and power densities of the devices, but also determinative of the stability of the electrodes and device. Introduction of unique electrolytes with wide electrochemical stability window such as WISE, molecular crowding electrolyte, and hydrate-melt electrolyte, into AHSCs is the most promising strategy to increase the energy density of AHSCs. In this context, however, in-depth understating of the ion transport mechanism and improvement in the ionic conductivity of these electrolytes are urgent to ensure the high power density of AHSCs. For the more comprehensive understanding of the electrochemical stability window and widened mechanism, and for promoting the interfacial charge transfer, interfacial phase at the two electrode sides should be carefully monitored and analyzed when using these electrolytes. Solvation structure is another important factor that determines the charge transfer of ions at the interface, as it significantly influences the interphase component and desolvation kinetics. Thus the design of optimized solvation structure of electrolytes is also of great importance in the future.

(4) With the increasing demand of energy storage devices in future smart society, consideration of the use effectiveness under different environments is urgent and highly desirable. The AHSCs using (quasi-)solid-state electrolytes will be the trend due to their safety and good mechanical robustness. However, we have to acknowledge the problem that the interfacial contact of solid electrolytes with electrode materials is generally limited in traditional sandwiched device architectures, which is not good for rapid charging/discharging of AHSCs. Integrated device architecture with (quasi-)solid-state electrolyte infiltrated into 3D electrode is of promising potential to address the above challenge. To this end, novel strategies toward the 3D integration need to be explored in future studies. More attention should also be paid to the interface engineering of electrode/electrolyte under bending, twisting, high/low temperature, external stress, and other real environments. Comprehensive understanding and complete solution of these issues are crucial to promote the design of multifunctional AHSCs for practical applications.

(5) Multivalent ion AHSCs using charge carriers of Zn^{2+} , Ca^{2+} , Mg^{2+} , Al^{3+} , etc. are very promising to deliver both high energy density and power density. However, this type of device is still at

the infant stage, and realizing high comprehensive performance of multivalent ion AHSCs is still quite a challenging task. For multivalent ion AHSCs using corresponding metal as the anode and capacitive materials as the cathode, the dendrite issue or/and sluggish plating/stripping kinetics of anode are the main obstacles to achieve high rate performance and power density. When capacitive anode is used for assembling multivalent ion AHSCs, the challenge is on the cathode side where multivalent metal ions should reversibly insert into/deinsert from battery-type electrode materials. Currently, such host materials are still lacking; in particular, the multivalent ion uptake generally leads to serious structural damage to the host materials due to the strong interactions with crystal lattice. Tremendous efforts should be devoted to stabilizing the host materials, while not deteriorating the ion diffusion ability.

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水系混合超级电容器先进电极材料与器件研究进展

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摘要 使用有毒、易燃有机电解液的传统电化学储能器件存在较大的安全隐患。相比之下, 新型水系混合超级电容器(AHSCs)具有更高的安全性和环境友好性。AHSCs作为水系电池和水系超级电容器之间的桥梁, 能够结合电池电极高的比容量和电容电极大功率和长寿命的优点, 有望与电池系统结合使用或者完全替代电池系统。在过去的几十年中, 研究者致力于开发先进的电极材料和设计结构新颖的水系混合电容器。然而, 全电池搭配时电池型电极和电容型电极存在容量和动力学不匹配的问题。本文从电池电极、电容电极和新型电解质的概念设计三个方面综述了AHSCs的研究进展, 讨论了具有“双离子”储能机制和非极性特性的多功能AHSCs, 并进一步阐述了多价AHSCs (特别是锌离子AHSCs)的最新进展及有待解决的关键问题。最后, 本文总结了AHSCs面临的挑战, 并对未来构筑更高功率密度和多功能AHSCs器件的发展方向作出了展望。