



Review article

Recent progress of cathode materials for aqueous zinc-ion capacitors: Carbon-based materials and beyond

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ABSTRACT

As an emerging multivalent-ion-based energy storage device, aqueous zinc-ion capacitors (AZICs) combine the merits of zinc-ion batteries with high energy density, excellent safety, low cost and environmental friendliness, and the advantages of supercapacitors with high power density and superior cycling performance. Therefore, AZICs have been considered as a new promising electrochemical energy storage system. Though great progress of AZICs has been made recently, they are still in the infant stage and face many challenges. Specially, the unsatisfactory energy density needs to be improved to realize their practical applications, which calls for high-capacity cathode materials. In this review, after a brief introduction of progress and mechanism for AZICs, we provide a systematical overview of the latest advances in the state-of-art cathode materials. The synthesis route, structure and morphology, electrochemical performance, energy storage mechanism as well as the merits and drawbacks of various cathode materials are comprehensively compared and discussed. Finally, a summary and outlook of the challenges and future perspectives of AZICs were presented. With these, this review might offer some guidance for the future design of dedicated novel cathode materials to realize the great potential of AZICs.

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1. Introduction

The wide spread applications of consumer electronics, electric vehicles and grid-scale energy storage demand continually the development of higher performance energy storage devices, like batteries, supercapacitors (SCs) and the hybrid systems [1–6]. Batteries, especially lithium-ion batteries, exhibit the advantages of high energy density, high working voltage and low self-discharge [7–10]. However, they suffer from poor power density, safety issues, and relatively short cycling life [3,11]. Supercapacitors, on the other hand, have the merits of high power output, long lifespan and broad working temperature [12–14]. But their low energy density severely limits their applications. Therefore, high-performance hybrid devices, the so-called metal-ion capacitors (MICs) which combine the advantages of batteries and SCs, are emerging as a novel energy storage system [15–17]. Typical MICs have a battery-type electrode to supply high energy and a capacitor-type electrode to deliver high power with metal salts dissolving in organic solvents as electrolyte [18]. The excellent performance and highly promising applications promote the great advances of MICs and lithium-ion capacitors (LICs) have even been commercialized by JM Energy Corporation of Japan. Recently, inspired by LICs, sodium/potassium-ion capacitors with similar device configuration and energy storage mechanism were also developed because of their low cost [16,17]. Nevertheless, the alkali metal-ion capacitors still face security risks of highly reactive Li, Na and K metals and the flammable and volatile organic electrolytes. Furthermore, the limited and the uneven distribution of lithium resources in the earth boosts the price and impedes the large-scale utilization of LICs [19]. Therefore, it is still highly demanded to develop safe, low cost, and green power sources with both high energy and high power densities [20].

With these in mind, various energy storage systems have been proposed, especially the multivalent metal-based batteries and capacitors [21–23]. Among these candidates, a lot of attention has been drawn to zinc-ion involved batteries and capacitors. The increasing interest in zinc-based energy storage devices could be ascribed to the distinct merits of zinc element, including its low redox potential (-0.76 V vs. the standard hydrogen electrode), excellent electric conductivity, high theoretical gravimetric capacity (823 mAh g^{-1}) and volumetric capacity (5855 mAh cm^{-3}), in addition to low cost and non-toxicity [24–29]. Unlike that of the reactive alkali metal-ion devices facing safety problem and other multivalent metal-ion devices suffering from relatively sluggish kinetics, zinc-ion related batteries and capacitors are considered to

be one of the most appealing energy storage systems for future large-scale applications because of their high safety, abundant resources, and long durability.

As a high-energy system, zinc-ion batteries (ZIBs) have been well studied and attractive electrochemical properties have been achieved [30–32]. Unfortunately, like other batteries, the poor power performance and inferior cycling life of ZIBs restrains their applications in many fields requiring fast charge/discharge and expanded lifespan. Therefore, much of the attention has been focused on zinc-ion capacitors (ZICs, also known as zinc-ion hybrid supercapacitors), which bridges the performance gap between ZIBs and SCs [33,34]. Like other MICs, typical ZICs are also composed of a battery-type electrode to provide high energy density and a capacitor-type electrode to ensure high power density with zinc salts-containing solution as the electrolyte. Specifically, carbon-based porous materials with a double-layer capacitive mechanism are the most commonly used cathodes, including activated carbon (AC) [35,36], biomass-derived carbon [37], and nanostructured carbon [38–40] et al. Zinc metal, featuring ultrahigh specific capacity, low cost and stable in air and water, can be directly used as anodes in ZICs [41,42]. In this case, ZICs store or release energy through a mechanism of the reversible ion adsorption/desorption on the surface of porous carbon and the fast deposition/stripping of Zn metal (Fig. 1a) [35,43]. There are also reports about layered transition metal compounds with a mechanism of fast intercalation/de-intercalation serving as anode materials [44]. Besides, some groups proposed a different configuration using transition metal compounds (*i.e.* MnO_2) with an intercalation pseudocapacitive energy storage mechanism as the battery-type cathode and, in this situation, AC was used as the capacitor-type anode [45,46]. For this configuration, ZICs demonstrate a different energy storage mechanism. As exhibited in Fig. 1b, this kind of devices store energy *via* a mechanism of electrostatic accumulation of charges on the AC surface (adsorption/desorption process) and Zn^{2+} intercalation/de-intercalation into/from MnO_2 channels [22,46]. In addition, the formation/dissolution of $Zn_4(OH)_6SO_4 \cdot nH_2O$ is supposed to be another way to store energy [47]. As for the electrolytes, aqueous solution dissolving zinc salts (such as $ZnSO_4$, $ZnCl_2$, and $Zn(CF_3SO_3)_2$) are most widely used because metallic Zn is supposed to be stable in neutral or slightly acidic solution and the as-fabricated aqueous ZICs would demonstrate a long-term cycling performance [22]. But the basic electrolytes are seldom applied due to the formation of zinc dendrites and insulating zinc oxide or hydroxide. In addition, novel aqueous electrolytes like hydrogel-based or water-in-salts-based electrolytes are

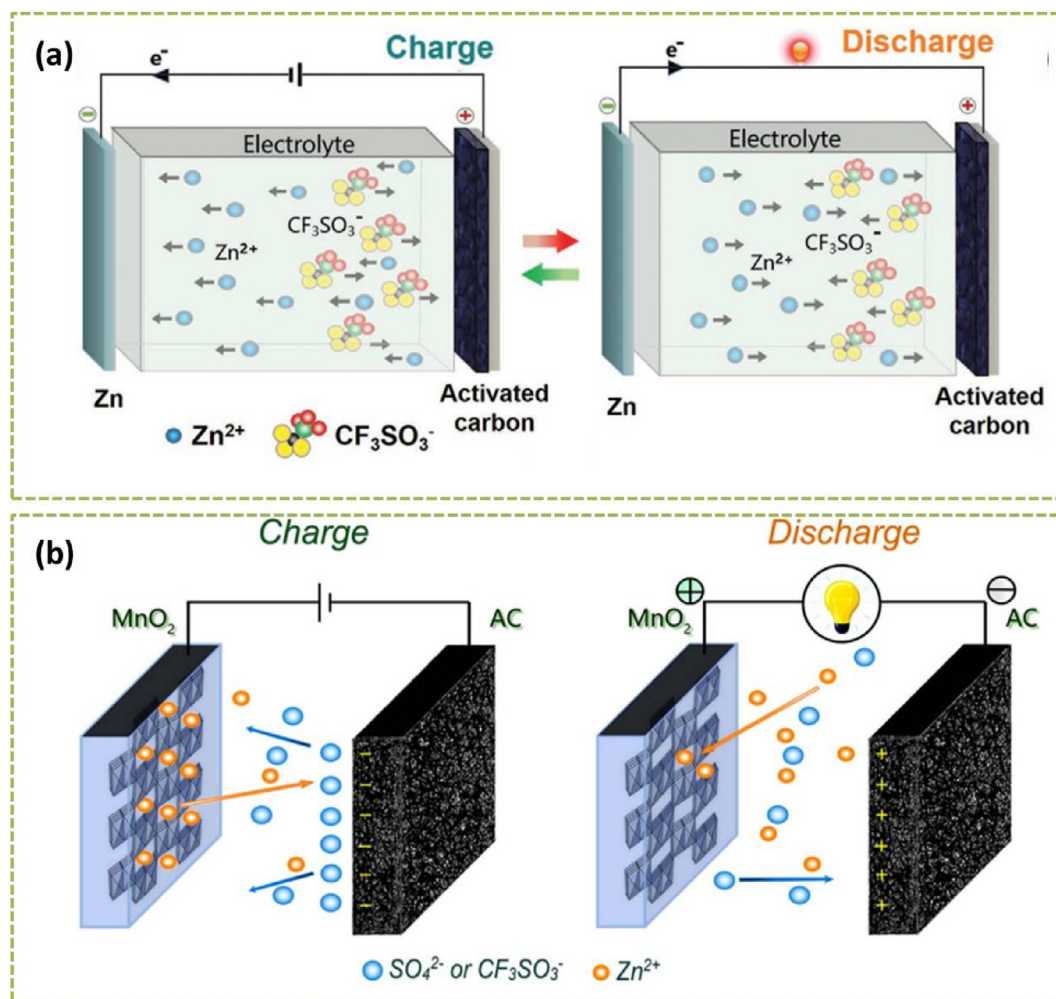


Fig. 1. Schematic of working mechanism of AZICs with a configuration of (a) Zn//AC (Reproduced with permission from Ref. [43]. Copyright 2020, Wiley-VCH.) and (b) MnO₂//AC (Reproduced with permission from Ref. [47]. Copyright 2019, Elsevier.).

adopted in ZICs because of the effective suppress of short-circuit risk [40,48–51]. The applications of organic electrolytes or ionic liquid electrolytes for ZICs were also reported [51–54]. However, considering the flammable and volatile of organic solvents and the high cost of ionic liquid, aqueous electrolytes with high ionic conductivity, environmental benignity and extreme safety are regarded to be the most promising and, thus, we will focus on the development of aqueous zinc-ion capacitors (AZICs) in this review.

Driven by the urgent demand of energy storage devices of high energy and power densities, low cost, high safety and long cycling life, AZICs have attracted much attention and exciting progress has been achieved since the first prototype [22,27,38,55]. However, the development of AZICs is still in the early stage and there are some critical problems which greatly hamper the practical applications of AZICs. First of all, the limited capacity of cathodes provides unsatisfactory energy density, which is more serious for carbon-based materials [55,56]. Secondly, the severe side reactions, the relatively sluggish dynamics and the notorious heterogeneous nucleation on the Zn surface during the stripping and deposition of Zn lead to a low power density and a short cycle life [32,57]. Last but not the least, like other MICs, AZICs also face the capacity which often results in a much lower energy density than expected, especially at a higher power output. Obviously, cathodes have become the

bottleneck to materialize the huge potential of AZICs. Hence, tremendous efforts have been devoted to design and fabricate cathode materials with novel morphology and structure, aiming to achieve high capacity and high power simultaneously. As shown in Fig. 2, various cathodes have been developed for high-performance AZICs, including carbon-based materials (i.e. activated carbons, nanostructured carbons and biomass derived carbons), transition metal-based compounds (i.e. metal oxides, nitrides and MXene) and other types of materials (i.e. phosphorene, g-C₃N₄ and polymers).

Moreover, as for the energy storage mechanism, it is well accepted that porous carbon-based cathodes demonstrate a highly reversible ion adsorption/desorption mechanism. But, researchers do not totally agree about the types of ions involved in the process. Some groups claim that anions from the electrolyte would be adsorbed on or released from the surface of porous carbon during charge and discharge, respectively [58,59]. Others deem that zinc ions also participate in the process [50,60,61]. Specifically, when working voltage is higher than the potential of zero charge (pzc), anions adsorption/desorption on the porous carbon surface is dominant, and when working voltage is lower than the pzc, it is mainly Zn²⁺ cations adsorption/desorption [22]. Therefore, the still controversial mechanism calls for deep understanding the energy storage process.

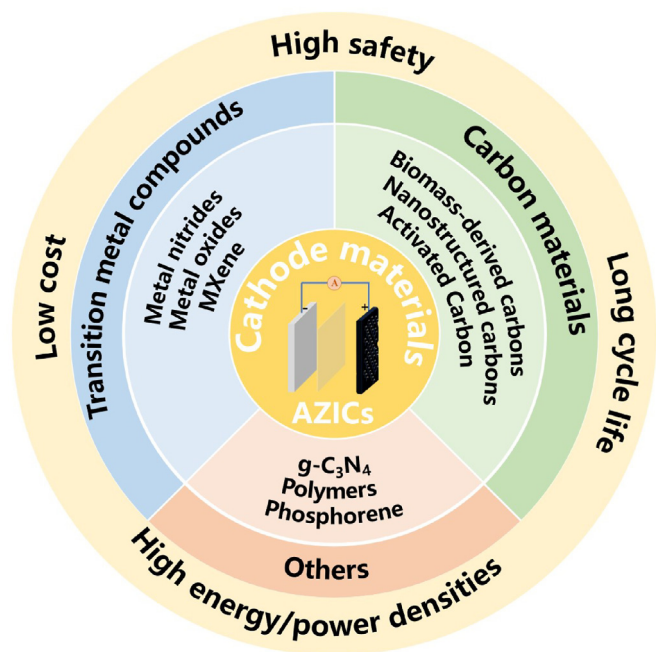


Fig. 2. Typical cathode materials for AZICs. (A colour version of this figure can be viewed online.)

With such great interests and also big challenges, a systematic review of the latest advances for cathode materials is highly needed to guide the future research. However, a comprehensive summary of cathode materials is still absent although some reviews did cover or refer to ZICs in some degree. For example, Dong et al. [22] have reviewed the progress of design concept, configuration and electrochemical behavior for multivalent metal ion batteries/capacitors. Also Li et al. [27] have reviewed the recent advances of ZICs with a focus on the charge storage mechanism. With the significance of cathode materials in AZICs and the related challenges, thus in this review, we will focus on the latest progress of cathode materials. The synthesis routes, structure and morphology, electrochemical performance, energy storage mechanism as well as the merits and drawbacks of various cathode materials will be comprehensively compared and discussed. Finally, an outlook will be presented to highlight the important challenges and possible directions for AZICs. We believe that this review will provide some constructive guidelines for scientists and the community towards high-performance AZICs in future.

2. Carbon-based cathode materials

Carbon-based materials have been extensively applied in batteries, SCs and hybrid ion capacitors due to their cost effectiveness, abundant resources, generally high electrical conductivity, excellent physical/chemical/electrochemical stability, rich surface chemistry and tunable structure [62–64]. It should be noted that some carbon allotropes have played a critical role in the current commercial energy storage systems, such as graphite in LIBs and AC in SCs. In particular, various types of porous carbon materials with high specific surface area (SSA) and novel structure have demonstrated exciting potential in MICs. Although Zn^{2+} has similar ionic radius as Li^+ , they show relatively much sluggish kinetics because of higher charge number [65]. Therefore, the structure, morphology and porosity of the cathode materials for AZICs should be elaborately designed to achieve high rate capability. Herein, the latest advances of activated carbons, nanostructured carbons and

biomass derived carbons as cathodes in AZICs are summarized, with an emphasis on their synthesis, structure, electrochemical properties and mechanisms.

2.1. Activated carbon

Activated carbon has been widely used in commercial SCs and can be facilely prepared in large scale from carbon-rich materials through a process of carbonization and physical and/or chemical activation [62]. Since the first report of hybrid supercapacitor using AC as cathode and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as anode [66], various types of AC have been thoroughly investigated in MICs [18,19,67–70], including the recently emerging AZICs [41,44,59].

2.1.1. Undoped activated carbon

Conventional undoped ACs are commonly used as cathodes in the early studies of AZICs. For example, Dong et al. designed AZICs using commercial AC, Zn metal foil and ZnSO_4 aqueous solution as the cathode, anode and electrolyte, respectively [71]. The Zn//AC devices demonstrate high electrochemical performances of an acceptable energy density of 84 Wh kg^{-1} , an ultrahigh power density of 14.9 kW kg^{-1} and an outstanding cycle life of 91% capacity retention over 10,000 cycles. Commercial AC was also applied as cathode by Boruah et al. to fabricate photo-rechargeable ZICs by paring with an optically and electrochemically active V_2O_5 nanofiber anode [72].

Nevertheless, traditional undoped AC suffers from low capacity ($<100 \text{ mAh g}^{-1}$) and inefficient energy/power density due to its pure physical adsorption/desorption charge storage mechanism, micropore dominated porosity, low SSA, inadequate electrical conductivity and poor wettability between the electrolyte and the electrode materials [12,13,48,73,74]. Possibly effective strategies to solve these issues are to develop novel carbon materials with suitable nanostructures or doping with heteroatom [75,76]. It should be noted that the morphology and structure of porous carbon play a crucial role in the electrochemical performance of energy storage devices [77]. Hierarchically porous carbons with well-designed structure and finely adjustable pores could effectively increase the accessible adsorption sites and facilitate mass transportation, thus enhancing the specific capacity and rate capability [78]. Moreover, carbon materials with heteroatom dopants or bearing heteroatom containing groups could provide extra capacity by fast and reversible Faradaic redox reactions [79].

Through adjusting the preparation process parameters, AC with advanced structure and finely tunable porosity could be obtained and, thus, high performance could be realized. For example, contrasted to the conventional AC materials prepared by one-step activation of carbon-rich precursors at high temperature, Zhou et al. [43] proposed an in-situ two-step activation method to construct a hierarchical porous AC (HPAC) and used it as cathode for AZICs. The specific preparation process includes two steps during carbonization and activation of asphalt with KOH. First of all, asphalt was pre-carbonized at 400°C to enhance the structural stability and to control the size distribution of nanopores while KOH activating agent could react with active carbon atoms generated by carbonization treatment to impede the interaction between active atoms and unsaturated bonds. Secondly, the fully activation and carbonization of asphalt was proceeded at a high temperature of 900°C to further enhance the structural stability and to improve the SSA. Therefore, the in-situ two-step activation strategy endows HPAC with a hierarchical porous structure mainly consisting of micropores and mesopores (Fig. 3a–b). The as-fabricated HPAC demonstrates a high SSA ($3525 \text{ m}^2 \text{ g}^{-1}$) and a large pore volume in combination with a reasonable pore size distribution (Fig. 3c–d), which is expected to provide abundant active sites and fast kinetics.

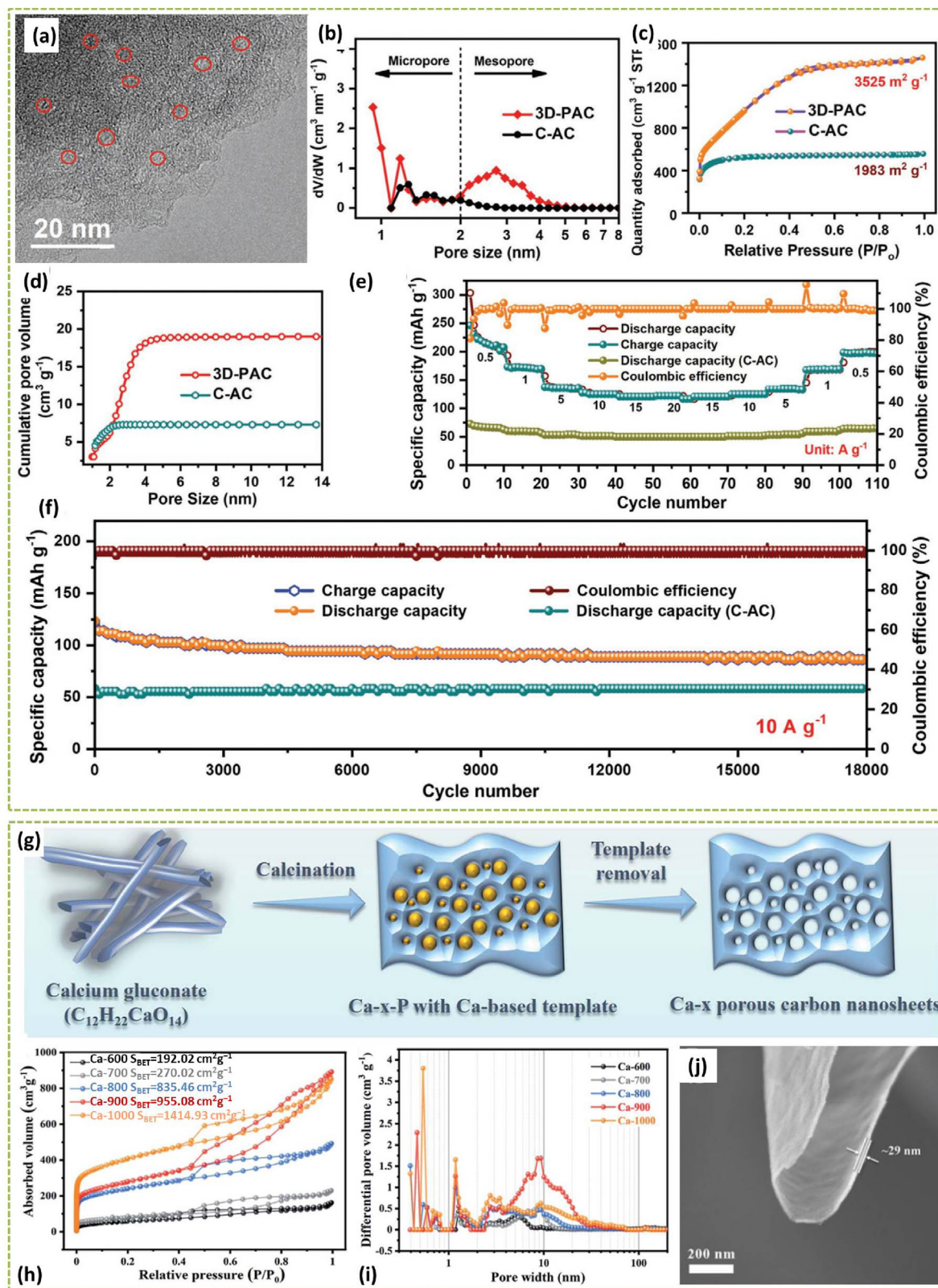


Fig. 3. (a) HRTEM image of HPAC; (b) pore size distribution, (c) nitrogen adsorption-desorption isotherms and (d) cumulative pore volumes of HPAC and C-AC; (e) Rate capability and (f) long-term cycling performance of AZICs based on HPAC and C-AC. Reproduced with permission from Ref. [43]. Copyright 2020, Wiley-VCH. (g) Schematic illustrations of the synthetic process of Ca-x; (h) nitrogen adsorption-desorption isotherms and (i) pore size distributions of Ca-x; (j) SEM image of Ca-900. Reproduced with permission from Ref. [80]. Copyright 2020, Royal Society of Chemistry. (A colour version of this figure can be viewed online.)

As shown in Fig. 3e–f, the HPAC cathode-based AZICs delivered a high capacity of 231 mAh g^{-1} at 0.5 A g^{-1} , an ultrafast rate capability of 119 mAh g^{-1} at 20 A g^{-1} , and a good cycling stability of $\sim 70\%$ after 18,000 cycles at 10 A g^{-1} , all of which are way better than those of commercial AC (C-AC).

In addition to physical/chemical activation, the template method is another typical strategy to prepare porous carbon with well-adjusted nanostructure. Recently, Zhang et al. [80] constructed ultrathin hierarchically porous carbon nanosheets as cathode for AZICs through an in-situ self-template method. With calcium gluconate as starting material and carbon source, the porous carbon nanosheets were facilely prepared by thermal treatment at certain temperatures followed by acid etching and water washing, as presented in Fig. 3g. By carefully adjusting the calcination temperature, the optimized product displays a structure of ultrathin porous nanosheets with a high SSA and well-balanced micropore, mesopore and macropore (Fig. 3h–j). Benefiting from these, AZICs using the as-obtained carbon nanosheets as cathode exhibits a high energy density of 75.2 Wh kg^{-1} and a stable cycling life with retention of 90.9% after 4,000 cycles. Besides, there are also reports about novel structured carbon materials for AZICs with satisfactory electrochemical performance, such as phenolic resin or waste polyurethane derived mesoporous carbons [57,81], and ethylenediaminetetraacetic acid tetrasodium salt hydrate derived three-dimensional (3D) porous activated carbon [82]. From the above-mentioned descriptions, nanostructured carbon materials are strong alternatives to conventional ACs due to their well-designed structure, elaborately tailored porosity, increased SSA, and enhanced electrical conductivity, which are critical factors to realize high energy and power densities. In addition, controllable porosity and acceptable tapping density should be received more attention to achieve high volumetric energy density.

2.1.2. Doped activated carbon

The capacity of porous carbon could be effectively enhanced by heteroatom doping which provides redox-active centers and deliver extra pseudocapacitance [83]. In addition, this strategy could also improve the electrical conductivity and wettability of these electrode materials, thereby achieving better rate capability [84]. For example, Lu et al. [61] designed a N-doped hierarchically porous carbon (HNPC) cathode with enhanced chemical adsorption of Zn^{2+} . As shown in Fig. 4a, HNPC was synthesized via two simple steps. Firstly, the carbon precursor was prepared with zeolite NaY as the template and furfuryl alcohol as the carbon source by a modified isostatic pressure-assisted impregnation process. Then the hard template was removed and the as-obtained sample was thermally annealed at 850°C under ammonia atmosphere in order to simultaneously introduce N dopants and generate hierarchical pores. The authors deemed that, revealed by both the experimental results and theoretical simulations, N doping enables the porous carbon with a series of fantastic features like good electrical conductivity, excellent surface wettability, and large electrochemically active surface area, which facilitates ion/electron transport and ensures sufficient space for Zn^{2+} storage. Thus, the as-prepared capacitors demonstrate an exceptionally large specific capacity (Fig. 4b), a high energy density (107.3 Wh kg^{-1}) and an extremely high power density (24.9 kW kg^{-1}). Moreover, compared with non-doped porous carbon (only 82.4%), an ultra-stable cycling performance was obtained with capacitance retention of 99.7% after 20,000 cycles for HNPC-based AZICs, exhibiting the advantages of doping (Fig. 4c). Another group reported AZICs consisting of oxygen-rich porous carbon cathodes and zinc anodes [85]. The porous carbons were facilely prepared through direct pyrolysis of pyromellitic acid tetra-potassium salt. The sample with optimized thermal treatment shows a hierarchical porous framework

composed of hollow nanocarbon spheres with rich carbonyl and hydroxyl groups. The as-assembled devices deliver a high capacity of 179.8 mAh g^{-1} in a wide operational voltage of 0–1.9 V, an energy density of 104.8 Wh kg^{-1} , and an ultrahigh power density of 48.8 kW kg^{-1} . The outstanding capacity and energy density are ascribed to not only the electric double-layer capacitance of porous carbon, but also the variation in oxidation states of oxygen functional groups and the reversible electrochemical hydrogen adsorption and desorption. Furthermore, a simple surface carbon coating was applied to suppress zinc dendrite growth and endows the devices with ultra-long cycling life of 30,000 cycles with an extremely high capacity retention of 99.2%.

There are also reports about bi-heteroatom doping to enhance the electrochemical properties of porous carbon. For instance, Lu et al. [48] proposed and designed a two-dimensional (2D) layered B/N co-doped porous carbon (LDC) via pyrolysis of H_3BO_3 /acrylonitrile copolymer composite (Fig. 4d). In the composite, H_3BO_3 acts as both an intercalator and B dopant for the carbon matrix while the highly stable backbone of copolymer provides high output of carbon and the side chain of nitrile group offers in-situ N doping. Consequently, B/N co-doping, the finely engineered 2D layered structure, high SSA and hierarchical porosity enable LDC with increased electrochemical active sites, short mass/charge transfer pathway and fast kinetics. As shown in Fig. 4e–f, the hybrid Zn//LDC devices demonstrate a high specific capacity (127.7 mAh g^{-1}), and outstanding energy (86.8 Wh kg^{-1}) and power (12.2 kW kg^{-1}) densities, significantly outperforming the non-layered carbons (LC). In addition, the device also presents a long lifespan of 6,500 cycles with the capacitance retention of 81.3% and a low self-discharge. Deng et al. [86] developed a novel N/O co-doped hierarchical porous carbon on carbon cloth (HPC/CC) with enhanced pseudocapacitance. HPC/CC was simply synthesized by uniformly drop-casting precursor solution of Zn-zeolitic imidazolate framework and polyacrylonitrile in DMF on the surface of carbon cloth, followed by thermal annealing at a desired temperature and acid etching process. Benefiting from the high SSA, interconnected porous conductive network with a suitable pore size distribution and, more importantly, the co-doping of N and O elements, the as-obtained self-standing HPC/CC-based device displays a high energy density of 110 Wh kg^{-1} , an attractive power density of 20 kW kg^{-1} , and a superb cycling life without obvious degradation after 10,000 cycles. Lee et al. [36] proposed a phosphorus and boron co-doped AC (P&B-AC) via an one-pot doping and calcining process and used it as the cathode for AZICs. Compared with the AC without doping, P&B-AC shows an enhanced electrical conductivity due to B-doping and an improved wettability due to P-doping. Therefore, by integration with Zn anode, the obtained device presents a high specific capacity of 169.4 mAh g^{-1} , a superb rate capability of 84.0 mAh g^{-1} at 10 A g^{-1} , and an ultra-long lifespan with capacity retention of 88% after 30,000 cycles. In addition, other types of heteroatom doped porous carbon cathodes for AZICs have also been reported, such as bimetal organic frameworks derived pyridinic nitrogen enriched porous carbon [56], B, N and O co-doped carbon flower [87] and oxygen-containing groups functionalized activated carbon cloth [88]. Obviously, doping is an effective strategy to increase the specific capacity, wettability and conductivity of carbon-based materials, which thus improve the energy and power densities of AZICs. Additionally, doping is a feasible method which could be easily applied in commercial products in large scale. However, doping with controllability and even distribution is still a big challenge. This obstacle might be overcome by mixing the precursors in a molecular level.

2.1.3. Other strategies to enhance the capacity of activated carbon

Some organic materials bearing functional groups could offer

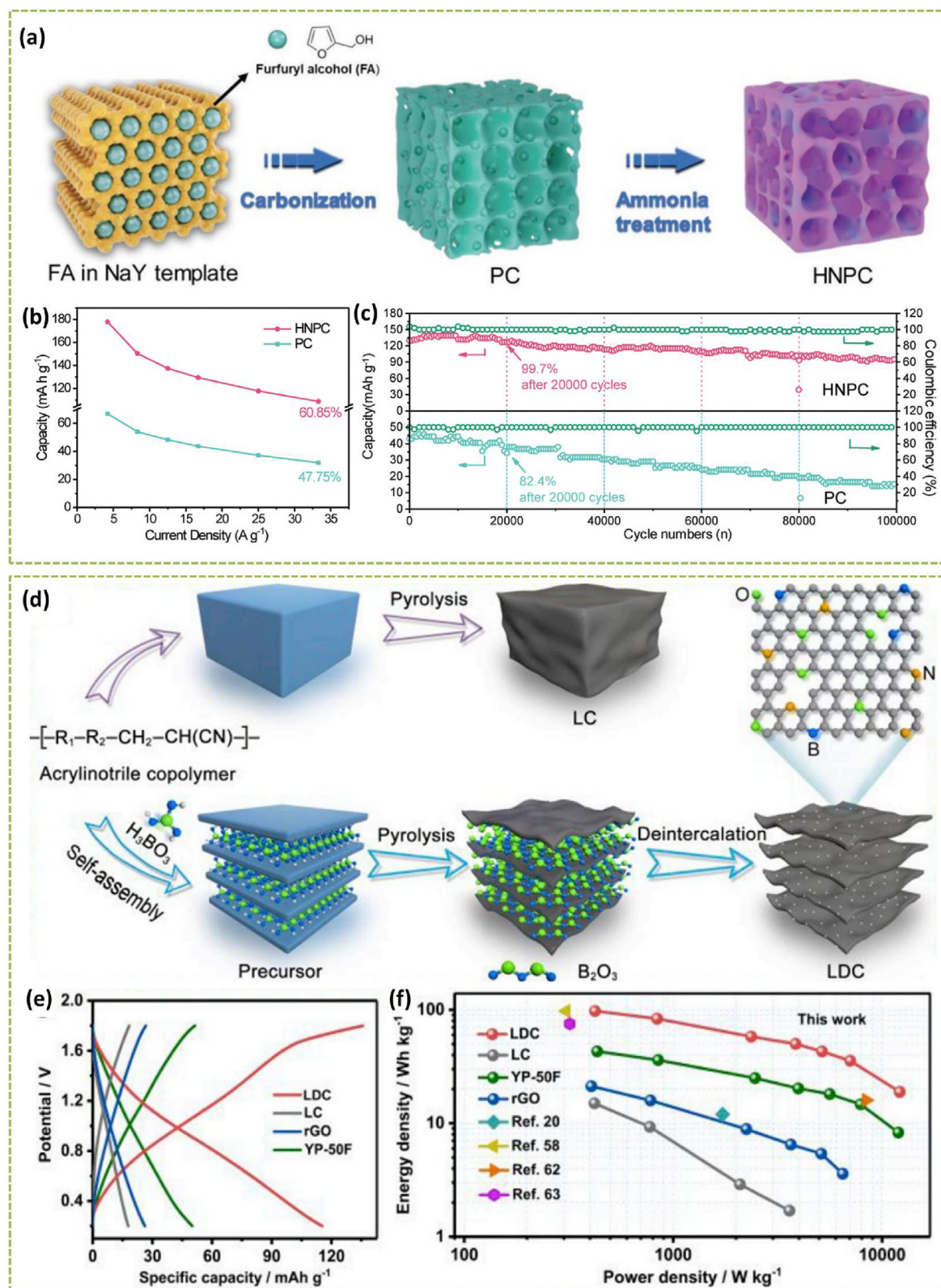


Fig. 4. (a) The illustration for the synthesis of HNPC; (b) specific capacity at different current density and (c) cycling stability of HNPC and PC. Reproduced with permission from Ref. [61]. Copyright 2019, Wiley-VCH. (d) Synthesis procedure of the non-layered carbon and layered B/N co-doped porous carbon; (e) galvanostatic charge-discharge curves at 0.5 A g⁻¹ and (f) Ragone plot of LDC based AZICs compared with other advanced aqueous ZHSs. Reproduced with permission from Ref. [48]. Copyright 2019, Elsevier. (A colour version of this figure can be viewed online.)

extra capacity by redox reaction. Therefore, modification with redox active materials is another strategy to improve the capacity of AC. Xin et al. [89] reported a poly(4,4'-thiodiphenol, TDP)-modified nanoporous activated carbon cathode for AZICs. The poly(4,4'-TDP)/AC cathode was prepared through two steps: 1) Nanoporous carbon was coated onto the carbon fiber cloth by the slurry-coating method; 2) TDP was electrodeposited onto the porous AC and the final product was obtained. The as-fabricated hybrid cathode shows not only electric double-layer capacitance from AC but also pseudocapacitance due to the introduction of redox-active polymer of poly(4,4'-TDP), which results in an approximately three-time increase of areal capacity compared with the bare AC cathode. Various small molecules and polymers with redox active groups could be chosen to improve the capacity of traditional ACs. This strategy illustrates a novel path to enhance the capacity of AC-based cathodes for AZICs. But, the unsatisfied stability of these materials during repeatedly charge/discharge process should not be ignored. One possible solution to this drawback is to fix the redox active materials on the surface of ACs by the covalent bonds.

Overall, conventional ACs have served as attractive cathodes in the early studies of AZICs due to their low cost and mature preparation process. However, the relatively low SSA and electrical conductivity of ACs limit their capacity and rate performance in AZICs. Based on the above discussion, we strongly propose to develop nanostructured carbon materials with sufficiently accessible surface area, abundant and hierarchical pores with rationally distributed size to ensure fast mass diffusion and numerous adsorption sites. Meanwhile, doping with heteroatoms or modification with polymers are also effective strategies to improve the ACs capacity by providing extra pseudocapacitance via fast redox reactions. Moreover, the electrical conductivity could be enhanced by regulating the porosity and increasing the graphitic degree.

2.2. Nanostructured carbon materials

One-dimensional (1D) carbon nanotubes (CNTs) and 2D graphene are two typical nanostructured carbon materials. Compared with traditional porous carbon materials, they show many attractive advantages in terms of electrical conductivity, SSA and physicochemical stability, making them excellent cathode and/or added conducting materials in advanced AZICs.

2.2.1. Carbon nanotubes

Benefiting the unique 1D structure and superior properties, CNTs have achieved exciting results in LIBs and SCs [90,91]. The previous reports demonstrate the potential application of CNTs in AZICs. For instance, Tian et al. [38] developed a ZIC using an oxidized CNTs (oCNTs) cathode and a zinc anode with ZnSO_4 contained liquid electrolyte and gel electrolyte. The oCNTs were synthesized with an improved Hummer's method by oxidizing CNTs firstly with H_2SO_4 and then KMnO_4 . The as-prepared aqueous hybrid ZIC exhibited a specific capacitance of 53 F g^{-1} and a stable cycling performance up to 5,000 times, which is better than the ZIC with the un-oxidized CNT cathode. The reason of the improved performance is that oCNTs cathode shows not only electric double layer capacitive behavior but also additional pseudocapacitance from the oxygen groups via a reversible Faradaic process. Besides directly used as active materials, CNTs could be excellent support for other cathode materials. More importantly, CNTs might find potential applications in flexible energy storage devices benefiting from their high length-diameter ratio. However, CNTs tend to agglomerate because of the high π - π interaction between each other, leading to inferior electrochemical performance. Consequently, surface modification of functional groups or surface coating with soluble materials could effectively solve this problem.

2.2.2. Graphene and reduced GO

Graphene, a single-layer carbon sheet with extraordinary physical and chemical properties, has demonstrated many appealing applications in energy storage and conversion systems since its discovery [92–95]. Considering its high theoretical SSA, high electrical conductivity and rich surface chemistry, graphene-based porous materials could be ideal cathode candidates for AZICs. Zhang et al. [96] constructed AZICs with Zn foil and activated microwave-exfoliated graphite oxide (a-MEGO). The a-MEGO with an extraordinarily large SSA and a high electrical conductivity was prepared by microwave irradiation of graphite oxide followed by KOH activation, as reported by Rouff's group [97]. The authors investigated the impacts of different Zn-containing electrolytes and the concentrations of the salts in the electrolytes on Coulombic efficiency (CE) of the as-fabricated Zn/a-MEGO capacitors. As displayed in Fig. 5a, among the various electrolytes, $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ demonstrates the best Zn stripping/plating efficiency with a stable value of over 90% after 15 cycles. This could be ascribed to the strong interaction between bulky CF_3SO_3^- anions and water molecules, which reduces the interaction between Zn^{2+} ions and the adjacent water molecules and thus suppresses the formation of byproducts during Zn plating and the unwanted hydrogen evolution. This result is consistent with the XRD patterns (Fig. 5b). No obvious byproduct was detected on the substrate during Zn plating in $\text{Zn}(\text{CF}_3\text{SO}_3)_2$. Additionally, a porous and interconnected Zn plating structure was revealed in $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ while plate-like particles with random orientations were observed in ZnSO_4 (Fig. 5c–d). The isolated plate-like Zn could result in poor electrical conductivity and formation of byproducts and thus leads to inferior CE. Benefiting from the high CE of $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ -based electrolyte and excellent a-MEGO-based cathode, the as-fabricated AZICs exhibit a significantly wide working voltage of 1.9 V, a high energy density of 106.3 Wh kg^{-1} and an ultrahigh power density of 31.4 kW kg^{-1} . Moreover, an ultra-long cycling life up to 80,000 cycles with a retention of 93% was obtained (Fig. 5e). As can be seen from the above results, graphene-based AZICs exhibit obvious advantages over the traditional porous carbons because of the improved SSA and conductivity.

Carbon materials doped by heteroatom or modified by functional groups have been proven to effectively improve the electrolyte wettability, Zn-ion chemical adsorption and pseudocapacitive redox activity [36,85,86]. Thus, reduced graphene oxide (rGO) bearing rich oxygen-containing groups is expected to show outstanding capacity and rate performance because additional pseudocapacitance can be realized through the fast redox reaction of the functional groups. Shao et al. [98] reported AZICs using chemically reduced graphene oxide as the cathode. As illustrated in Fig. 6a, the residual oxygen functional groups with strong electronegativity play a critical role in the charge storage capability of rGO, including providing extra pseudocapacitance by introducing rapid redox reactions at/near sheet surface, improving the hydrophilic feature of the electrode, and reducing the Zn-ion adsorption energy barrier to help forming electrostatic EDLC. The types and content of oxygen functional groups of rGO could be systematically regulated by different types of chemical reduction methods and reducing agents (Fig. 6b). It must be pointed out that the oxygen functional groups are always accompanied with structural defects and different reducing agents have a critical impact on the electrical conductivity of the obtained materials (Fig. 6c). Therefore, the oxygen-functional substituents and the reduction level should be well balanced to obtain high capacity and high rate capability cathode materials. The rGO cathode prepared by hydrogen peroxide assisted hydrothermal reduction shows the highest specific capacitance of 277 F g^{-1} because of the optimal surface functional oxygen groups and conductivity. More importantly, an

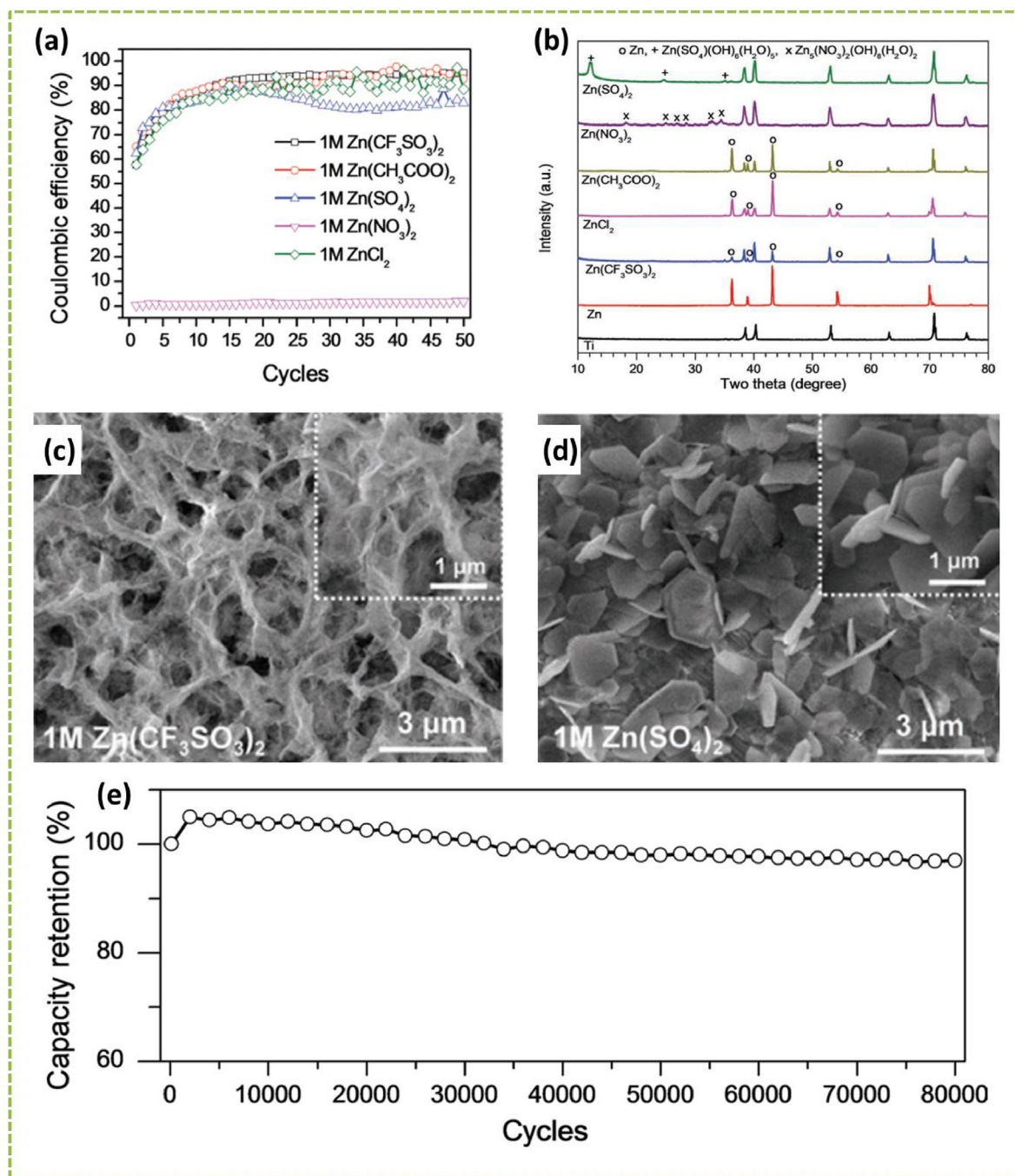


Fig. 5. (a) Zn stripping/plating efficiency and (b) XRD patterns of pristine Zn and Ti foils, and Ti foils with Zn layer plated in various Zn-based electrolytes; SEM images of Ti foils with Zn layer plated in (c) $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ and (d) ZnSO_4 electrolytes; (e) cycling stability of the Zn-aMEGO hybrid supercapacitors cycled at 8 A g^{-1} . Reproduced with permission from Ref. [96]. Copyright 2019, Wiley-VCH. (A colour version of this figure can be viewed online.)

outstanding capacitance retention of 97.8% is achieved after 20,000 cycles in ZnSO_4 electrolyte by pairing with Zn anode (Fig. 6d). Reduced GO shows great potential as high-capacity cathode because of the extra capacitance provided by oxygen-containing groups. In order to obtain high conductivity, the amount of these functional groups needs to be carefully tailored.

2.2.3. Graphene-based composites

Graphene or rGO sheets with large conjugated planes tend to stack with each other, which severely decreases the actual SSA and blocks the ions transportation. Compositing rGO with carbon

nanotubes could effectively solve the stacking problem [99]. As displayed in Fig. 7a, Zhang et al. [100] demonstrated high surface area and conductive reduced graphene oxide/carbon nanotube (rGO/CNT) composite fibers prepared by hydrothermally assembling of rGO and CNTs and then used them as cathodes in zinc-ion fiber capacitors (ZnFCs). The introduction of CNTs significantly prevents the restacking of rGO nanosheets and is also helpful to increase the electrical conductivity of the composite fibers. Hence, the specific capacity and rate performance could be improved due to the large ion accessible surface area and high electrical conductivity. With Zn coated graphite fibers as the anode and ZnSO_4 -

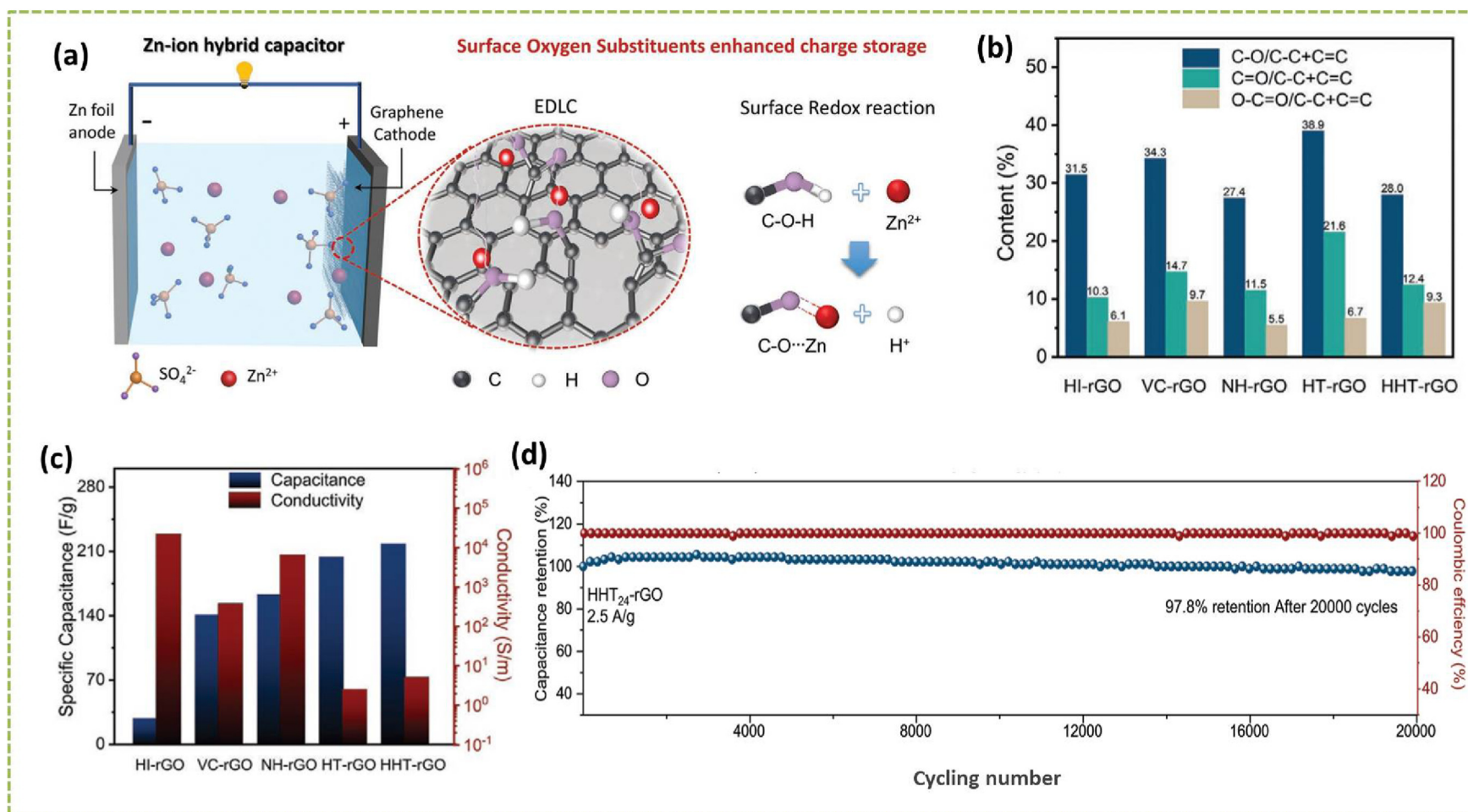


Fig. 6. (a) Schematic of the configuration, mechanism of the rGO cathode based Zn-ion hybrid capacitor with emphasis of the surface oxygen substituents' enhanced EDLC and surface redox pseudocapacitive charge storage; (b) oxygen functionalities ratio and (c) specific capacitance and electric conductivity under different scan rates of rGO prepared via different reduction methods; (d) cycling stability of HHT₂₄-rGO based AZICs. Reproduced with permission from Ref. [98]. Copyright 2021, Wiley-VCH. (A colour version of this figure can be viewed online.)

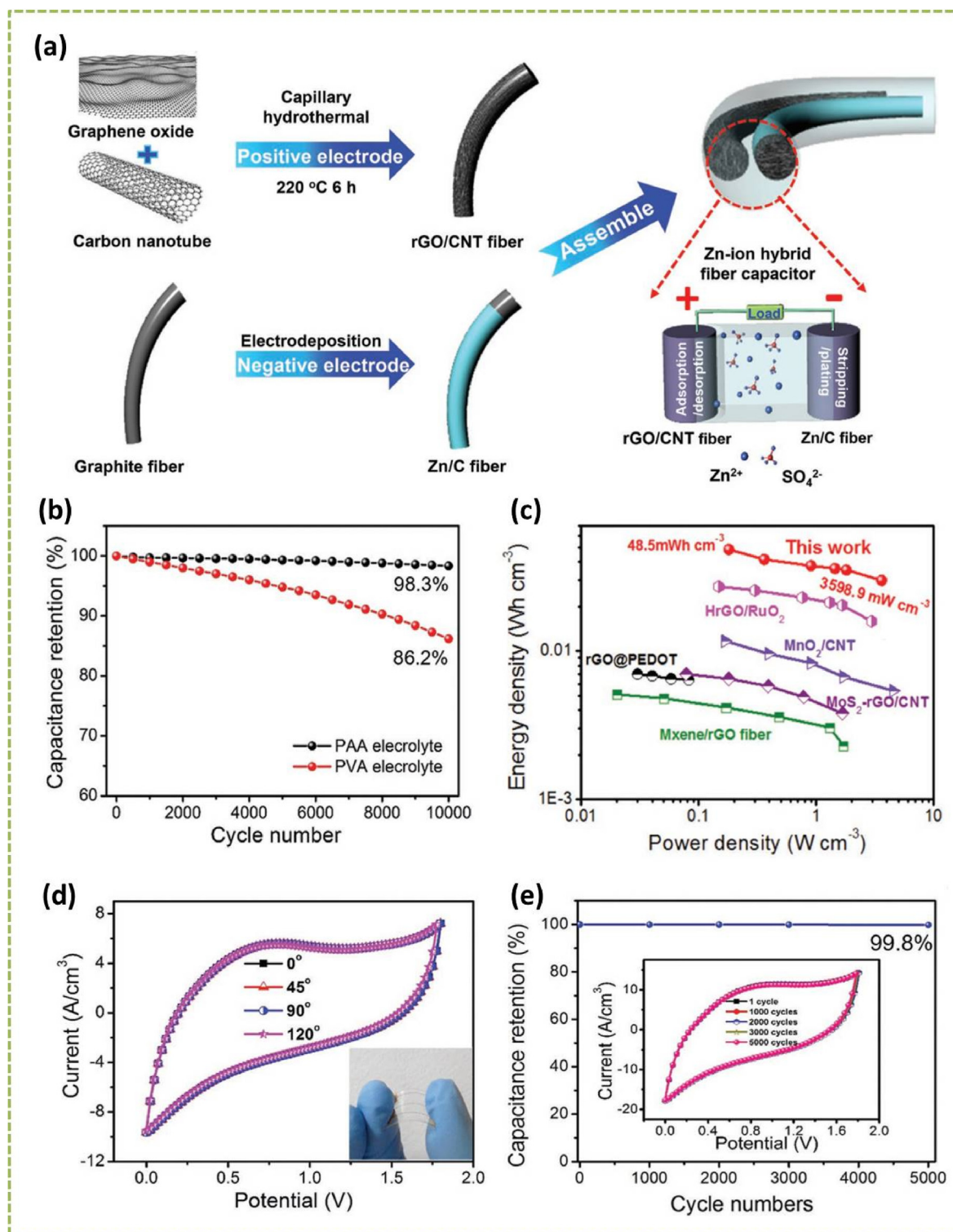


Fig. 7. (a) Schematic illustration of the synthesis of rGO/CNT and Zn-coated graphite fibers for assembling a Zn-ion fiber capacitor and the energy storage mechanism; (b) the comparison of cycling stability of the ZnFCs using ZnSO₄/PAA and ZnSO₄/PVA electrolytes; (c) Ragone plots of the ZnFCs in this study in comparison with other reported FCs; (d) CV curves of the ZnFC-PAA when bent at different angles; (e) capacitance retention of the ZnFC-PAA when bent to the 90° for 5,000 times (the inset shows the corresponding CV curve). Reproduced with permission from Ref. [100]. Copyright 2019, Wiley-VCH. (A colour version of this figure can be viewed online.)

filled polyacrylic acid (PAA) hydrogel as the quasi solid-state electrolyte, rGO/CNT cathodes based ZnFCs delivered a superb stable cycling stability and high energy and power densities, benefiting from the high electrical conductivity and abundant ion accessible

surface of rGO/CNT fibers in combination with high water-holding capability, high ionic conductivity and reduced interfacial resistance of PPA hydrogel electrolyte (Fig. 7b–c). The flexibility of the devices was also tested. As shown in Fig. 7d, similar cyclic

voltammetry curves were observed when bending the whole device at different angles, demonstrating the outstanding flexibility. Moreover, the device displays an excellent mechanical stability with a capacitance change of less than 0.2% after repeatedly bending to 90° for 5,000 times (Fig. 7e), showing promising applications in wearable electronics. Another group designed a multiwalled carbon nanotubes–reduced graphene oxide (MWCNTs-RGO) fiber by wet spinning of MWCNTs-RGO solution and used it as capacitor-type electrode for ZICs by pairing with Zn deposited MWCNTs-RGO anode [40]. The as-prepared fiber ZICs with an excellent self-healability of poly(vinyl alcohol)/Zn(CF₃SO₃)₂ aqueous gel electrolyte shows desirable energy and power densities in addition to a good flexibility.

Besides, functionalizing rGO with redox-active organic molecule is also effective to prevent agglomeration and thus enhance the capacitance. Xu et al. [101] reported an ultrahigh areal capacitance AZICs by adopting p-phenylenediamine covalently grafted rGO films (RGO@PPD) as cathode. Using PPD as a reducing and functional agent, the self-supporting RGO@PPD films were successfully fabricated through the solvothermal reaction, during which the PPD were covalently bonded to the surfaces of GO sheets via the acylation and ring-opening reactions. As a redox-active spacer, PPD not only helps to impede the restacking of graphene sheets to enhance the electrical double layer capacitance, but also provides extra pseudocapacitance by a reversible redox reaction. Thanks to the introduction of PPD, the functional RGO film-based AZICs displays tremendously high areal capacitance and energy density. Due to the 2D and flexible structure, rGO could serve as excellent substrates or building blocks to form 3D composites. The obtained composites have several advantages, including keeping the outstanding properties of graphene, increasing the accessible surface area and reducing the overall cost.

As two typical nanostructured carbon materials, both CNTs and graphene demonstrate excellent electrochemical performance as cathodes for AZICs because of their inherently high electrical conductivity, high SSA and unique 1D/2D structure. Nevertheless, severe agglomeration and restacking significantly reduce the real SSA and block the ion transport path, resulting in lower capacity and unsatisfactory rate capability. Besides, their high cost also hinders the wide applications. In light of these disadvantages, fabricating advanced composites with optimal structure, morphology and interaction is a feasible and highly promising method. Furthermore, the practical applications of nanostructured carbon materials are impeded by their low tapping density due to high SSA and large volume. For example, 3D graphene-based porous materials usually have extremely low density [102,103]. Consequently, Yang and co-workers proposed a capillary drying method to prepare 3D porous but compact graphene-based materials, providing a possible way to overcome this problem [92].

2.3. Biomass-derived porous materials

Benefiting from the low cost, easy accessibility, diverse structure, and facile fabrication process, biomass-derived porous carbon materials for electrochemical energy storage devices have received much attention [104–106]. For instance, Li et al. [58] produced porous carbon (PSC-Ax) with a well-defined architecture by pyrolysis of pencil shaving and then activation at the desired temperature (Fig. 8a). By pairing the optimized PSC-A600 with cheap Zn foil, high-performance zinc-ion capacitors were assembled, which display a highest energy density of 147.0 Wh kg⁻¹ and a maximum power density of 15.7 kW kg⁻¹ (Fig. 8b). Furthermore, the electrochemical performance with different mass loading was also investigated. As shown in Fig. 8c, the as-fabricated device could still work well at a mass loading of 24 mg cm⁻² with a capacitance

of over 200 F g⁻¹. By applying a biomass kelp-derived carbon as the cathode, Zeng et al. [107] designed a flexible solar-chargeable self-powered device based on in-plane printed Zn-ion hybrid micro-capacitor. As demonstrated in Fig. 8d, kelp-based porous carbon could be easily prepared by the conventional two carbonization and activation steps. The as-prepared kelp-carbon possesses a hierarchical, porous, and 3D interconnected micro-/nano-architecture with a high SSA of 3027 m² g⁻¹ and a pore volume of 1.87 cm³ g⁻¹ (Fig. 8e–f). The novel nanostructure enables the fabricated in-plane quasi-solid-state ZICs with high energy density, long lifespan and, more importantly, outstanding energy conversion/storage efficiency after being integrated with organic solar cells. Similarly, Wang et al. [108] fabricated a sustainable pine needles-based porous carbon cathode for AZICs with an effective activation technique. Specifically, pine needles were activated by potassium thioacetate which served as both the activator and the S source. By adjusting the activation temperature, S-doped 3D porous carbon (S-3DPCs) with high SSA and hierarchical pores can be obtained. Benefiting from the large accessible surface area and abundant doped active sites, the as-built AZICs demonstrate a high capacity of 203.3 mAh g⁻¹ and a maximum energy density of 162.6 Wh kg⁻¹. As we can see from the above results, biomass-derived porous carbons should receive special attention for their merits of abundance and renewability.

As a summary of the previous reports, various carbon materials including ACs, nanostructures carbons and biomass-derived carbons have been studied as cathodes in AZICs and great progresses have been made. However, there is still a big gap between the electrochemical performances of current carbon-based cathodes and the commercial requirements. For instance, the relatively low SSA and many inaccessible small and deep pores of commercial ACs leads to unsatisfactory capacity despite their advantages of low cost and mature manufacturing technology. Moreover, the structure of AC is seriously destructed during the activation process, resulting in decreased electrical conductivity and consequently poor power density. Biomass-derived porous carbons face similar challenges as commercial ACs although they have the merits of abundant raw materials and renewability. Nanostructured carbons like CNTs and graphene have received intensive attention because of their inherently high electrical conductivity and unique one-/two-dimensional structure with large aspect ratio. But they suffer from aggregation and self-restacking problems, not to mention the high cost and complex fabrication process. Hence, the morphology, porosity and surface chemistry of carbon-based materials should be well designed to obtain high capacity, high rate and stable cycling performance.

According to the physical adsorption/desorption dominant energy storage mechanism of capacitor-type electrode, the capacity is positively influenced by the accessible SSA and rich porosity with rational pore size distribution is beneficial for rapid electrolyte diffusion and could thus improve the rate performance. Therefore, the synthesis method, precursor selection and activation parameters need to be thoroughly investigated to regulate the morphology and porosity of carbon materials, aiming to increase the effective SSA and form a hierarchical porous structure. On the other hand, carbon materials usually suffer from low tapping density because of their highly porous structure, especially for CNTs and graphene. Based on this reason, more solvents and binders are needed to fabricate stable coating slurry and the coating layer tends to peel off the current collector in the pressing process. In such a situation, not only unsatisfactory volumetric capacity (corresponding to low volumetric energy density), but also inferior rate capability and poor cycling stability appear. Therefore, a good regulation of porosity and density should be emphasized. Besides, surface engineering should be given more attention to increase the active sites.

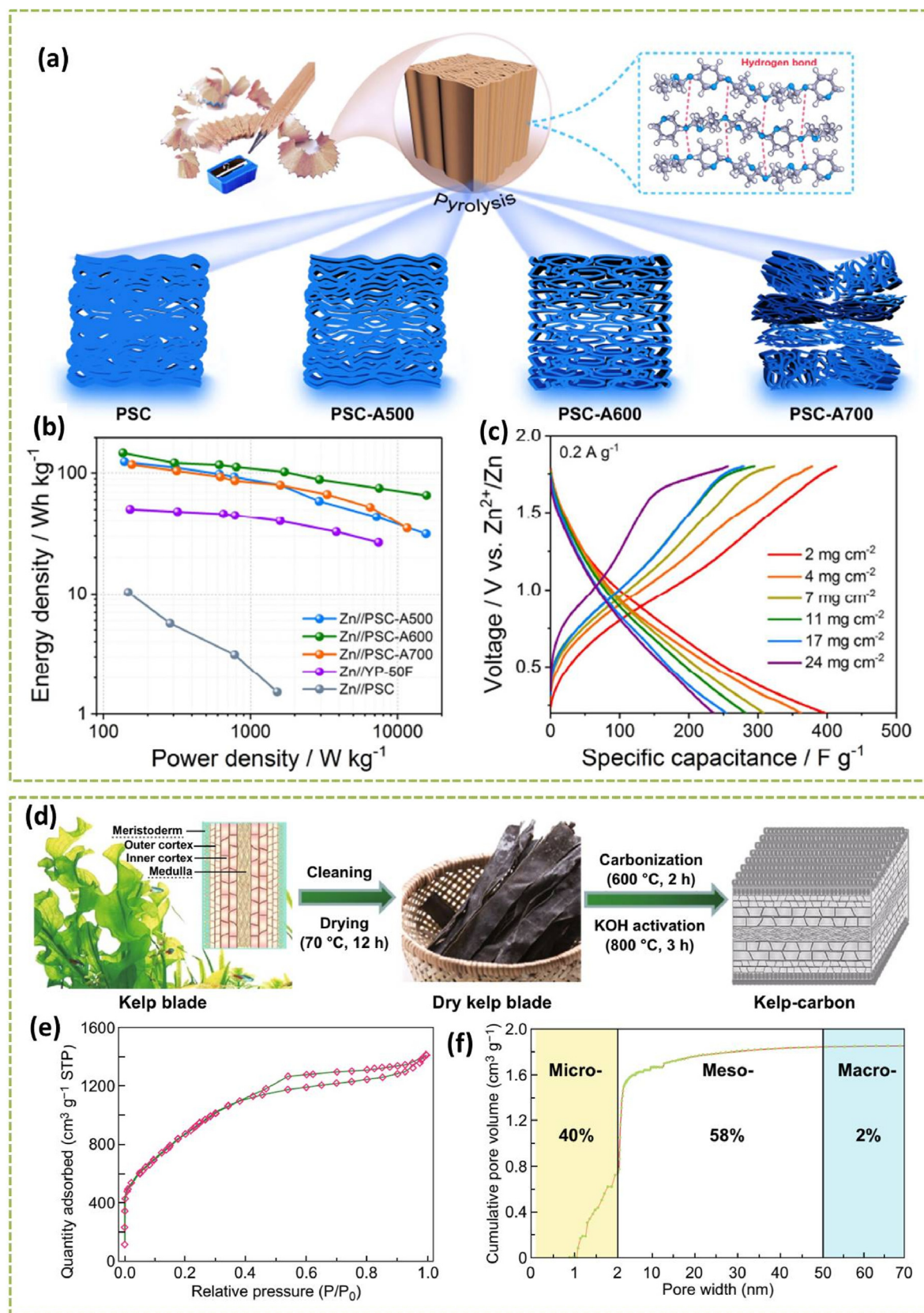


Fig. 8. (a) Schematic preparation of PSC and PSC-Ax; (b) Ragone plots for PSC and PSC-Ax; (c) GCD curves of the PSC-A600 under various mass loadings. Reproduced with permission from Ref. [58]. Copyright 2020, Elsevier. (d) Schematic preparation process of kelp-carbon; (e) N_2 adsorption/desorption isotherm and (f) pore size distribution of the kelp-carbon. Reproduced with permission from Ref. [107]. Copyright 2020, Springer. (A colour version of this figure can be viewed online.)

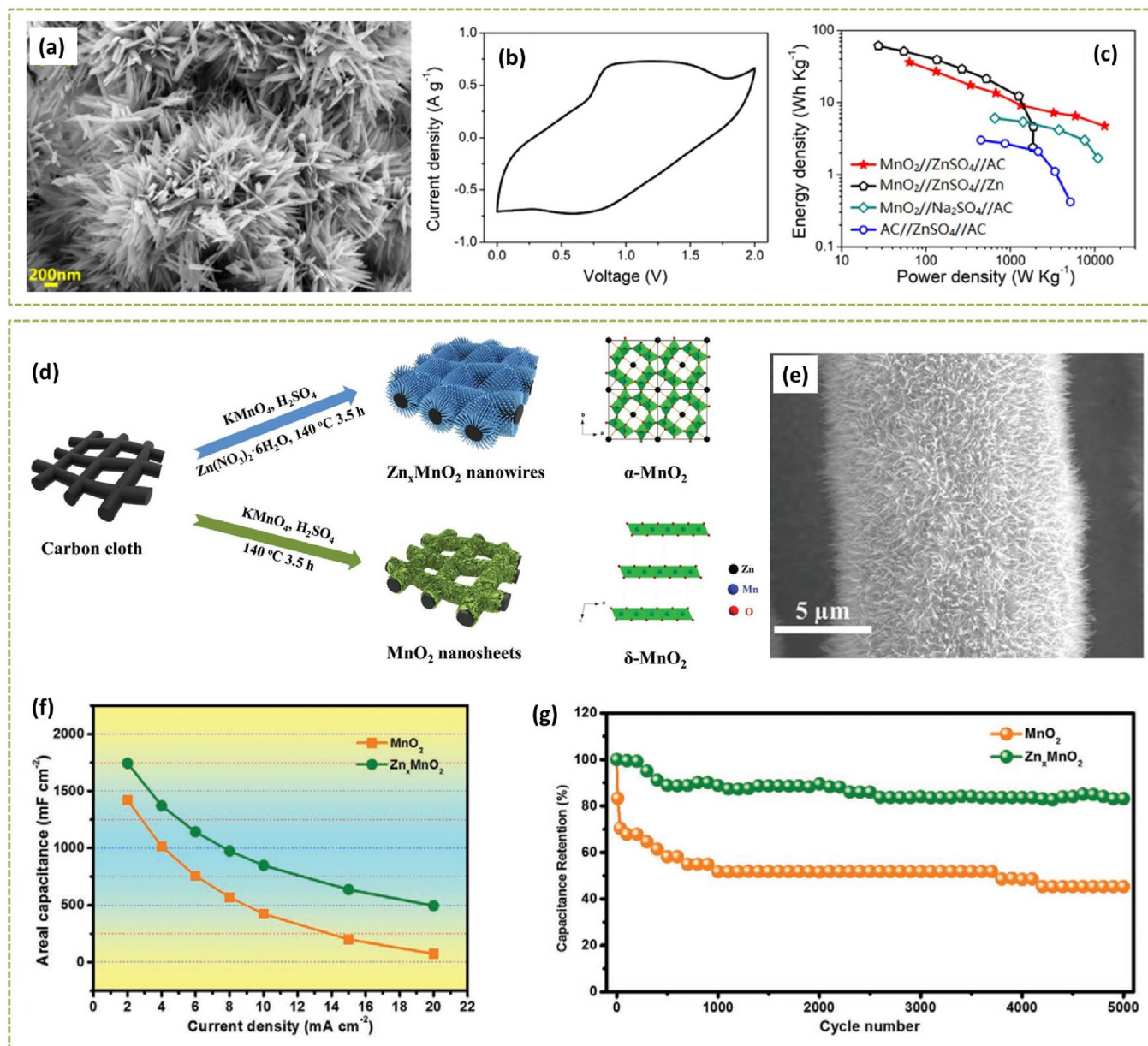


Fig. 9. (a) SEM image of the synthesized MnO₂ nanorods; (b) CV curve (at 10 mV s⁻¹) and (c) Ragone plots of MnO₂ nanorods//2 M ZnSO₄ (aq)//AC AZICs with comparison with ZIBs, asymmetric supercapacitor and symmetric supercapacitor. Reproduced with permission from Ref. [47]. Copyright 2019, Elsevier. (d) Schematic illustration of different reaction processes of MnO₂ nanosheets and Zn_xMnO₂ nanowires; (e) SEM image of the Zn_xMnO₂ nanowires; (f) Areal capacitance as a function of the current density and (g) cycling performance of the MnO₂//ACC and Zn_xMnO₂//ACC. Reproduced with permission from Ref. [46]. Copyright 2020, Wiley-VCH. (A colour version of this figure can be viewed online.)

Heteroatom doping or modification with redox active groups is a facile but effective strategy to enhance the capacity of carbon-based cathodes by providing extra pseudocapacitance and promoting the chemisorption of Zn²⁺ on the electrode surface. Furthermore, the enhanced wettability and electrical conductivity by doping could also improve the rate capability of carbon materials. But the cycling stability might become worse if high degree of doping and surface functionalization is adopted, which thus should be carefully balanced. Forming composites is another promising method to fabricate high-performance carbon cathodes for AZICs. Especially, 2D graphene is an excellent substrate to load other materials and also good building block to form 3D porous composites. For example, by compositing graphene with ACs, the high cost and restacking problems of graphene and the low SSA of ACs could be well solved. Recently, redox active small organic molecules and

polymers are receiving growing attention due to their high capacity derived from rapid redox reaction. However, they usually face challenges of inferior power density and limited cycling life because of low conductivity and structural instability. Fortunately, these drawbacks could be overcome by introduction of graphene to form composites.

3. Transition metal compounds-based cathode materials

Besides carbon-based porous materials, transition metal compounds, including metal oxide/nitride and MXene, can be also utilized as cathodes for AZICs. Similar to their applications in ZIBs, these pseudocapacitive materials store/release Zn²⁺ via a battery-type redox behavior [109,110]. Generally, the pseudocapacitive behaviors comprise two main charge storage mechanisms of

surface redox pseudocapacitance and intercalation pseudocapacitance, which contributes to high energy and power densities.

3.1. Metal oxides

Many metal oxides have been utilized as cathode materials for aqueous ZIBs and several show a potential in AZICs, including manganese oxides, vanadium oxides, and ruthenium oxide [111,112]. Specially, manganese oxides have been intensively explored as cathodes in ZIBs because of the advantages of natural abundance, low cost, low toxicity, and multiple valence states of Mn element [113–117]. These previous reports demonstrate that manganese oxides could be a competitive battery-type cathode for AZICs by paring with AC anode. For example, Ma et al. [47] proposed a novel configuration AZICs with MnO_2 nanorods as the cathode, commercial AC with high SSA as the anode and Zn^{2+} -containing aqueous solution as the electrolyte. Through a co-precipitation of MnSO_4 and $(\text{NH}_4)_2\text{S}_2\text{O}_8$, high crystallinity MnO_2 nanorods were fabricated with a diameter of 20 nm (Fig. 9a). As shown in the CV curve (Fig. 9b), a pair of redox peaks ascribed to Zn^{2+} insertion/extraction into/from the MnO_2 nanorods is observed in the operational potential of 0–2 V. This battery-like reaction mechanism is distinctly different from fast surface redox reaction involved in traditional asymmetric supercapacitors. Consequently, the $\text{MnO}_2//2 \text{ M ZnSO}_4//\text{AC}$ ZIC delivered an energy density of 34.8 Wh kg^{-1} , which is comparable to $\text{MnO}_2//2 \text{ M ZnSO}_4//\text{Zn}$ zinc-ion battery and significantly superior to $\text{MnO}_2//1 \text{ M NaSO}_4//\text{AC}$ asymmetric supercapacitors and $\text{AC}/2 \text{ M ZnSO}_4//\text{AC}$ symmetric supercapacitors (Fig. 9c), demonstrating the advantages of MnO_2 -based AZICs.

Nevertheless, the intrinsically poor electrical conductivity and the unstable structure when intercalated Zn^{2+} of MnO_2 negatively influence the electrochemical performance. To improve the electrical conductivity of MnO_2 , Wang et al. [45] assembled AZICs with free-standing MnO_2 -CNTs cathodes and MXene anodes. The MnO_2 -CNTs electrodes were facilely fabricated by filtration of the homogeneously mixed MnO_2 nanowires and CNTs solution with appropriate mass ratio and a similar method was applied to prepare MXene electrodes. Undoubtedly, the specific capacity of MnO_2 -CNTs was largely increased due to the improved electrical conductivity by introducing CNTs. To enhance the structural stability and the charge/discharge rate, one effective strategy is pre-intercalation of other ions into the tunnel structure of MnO_2 [115,118]. Chen et al. [46] reported AZICs with Zn^{2+} stabilized MnO_2 nanowires (Zn_xMnO_2) on mechanically flexible carbon cloth as the cathode and activated carbon cloth (ACC) as the anode. As shown in Fig. 9d, tunnel structured Zn_xMnO_2 nanowires were prepared and uniformly covered on the surface of the carbon cloth through a one-step hydrothermal process (Fig. 9e). The pre-intercalation of Zn^{2+} enables Zn_xMnO_2 with a high stability, which endows the cathode with a higher areal capacitance and a longer cycling life than that of pristine MnO_2 (Fig. 9f–g).

Vanadium oxides like V_2O_5 feature high capacity and fast kinetics for Zn^{2+} storage, rendering them competitive cathode candidates for ZIBs and AZICs [119,120]. For example, Zhao et al. [121] presented V_2O_5 -based cathode for AZICs by paring it with commercial AC. The XRD data clearly demonstrates the reversible intercalation/de-intercalation of Zn^{2+} into/from the layer of V_2O_5 . The $\text{AC}/\text{V}_2\text{O}_5$ shows a high capacity, but a relatively low energy density and an inferior cycling stability. Further investigation needs to be carried out to improve the storage performance, such as preparation of layered nanosheets by nanostructure engineering and enhancing the ion diffusion rate by pre-intercalation with other ions [122,123].

As described above, MnO_2 suffers from poor electrical

conductivity and manganese dissolution issues causing inferior rate capability and unsatisfactory cycling stability while the high toxicity of V-based materials impedes its applications. Therefore, other metal oxides with higher electrical conductivity and more stable structure have been developed. For instance, RuO_2 has been commonly used as pseudocapacitor material because of its high specific capacity, good rate performance and long lifespan [124,125], making it a promising cathode. Therefore, Dong et al. [126] assembled AZICs with amorphous $\text{RuO}_2 \cdot \text{H}_2\text{O}$, Zn metal and $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ as the cathode, anode and aqueous electrolyte, respectively. The $\text{Zn}/\text{RuO}_2 \cdot \text{H}_2\text{O}$ capacitors display outstanding electrochemical performance, such as a fast charge/discharge rate (36 s), a high power density (16.74 kW kg^{-1}), a high energy density (82 Wh kg^{-1}) and a superior cycling stability (87.5% retention after 10,000 cycles). The excellent rate property originates from the pseudocapacitive behavior energy storage mechanism and high conductivity of the amorphous $\text{RuO}_2 \cdot \text{H}_2\text{O}$. It should be noted that the structural water in the amorphous $\text{RuO}_2 \cdot \text{H}_2\text{O}$ is very important for Zn^{2+} storage because it can facilitate fast ion transport and, thus, much higher capacity and rate performance than those of the anhydrous RuO_2 could be obtained.

With the booming advances of ZIBs and ZICs, many metal oxides, especially for the Mn-/V-based compounds, have been investigated as cathodes because of their high capacity, multiple redox states and abundance. However, the unsatisfactory rate and cycling performances because of unstable structure and inferior electrical conductivity should not be neglected. To improve the stability, one of the most promising approaches is to pre-intercalate the metal oxides with other ions or compounds. Moreover, forming composites with highly conductive nanostructured carbons (i.e. CNTs or graphene) is the most possible solution to improve the low conductivity. Thus, we speculate that future research should focus on these two directions.

3.2. Metal nitrides

Titanium nitride (TiN) serves as an important intercalation pseudocapacitive material in the field of energy storage due to its excellent mechanical properties, high electrical conductivity and good chemical/electrochemical stability [127,128]. Huang et al. [129] adopted TiN as cathode materials in a Zn/TiN capacitor and evaluated the effects of various anions carriers on the electrochemical behaviors of intercalation pseudocapacitor materials. As shown in Fig. 10a, TiN consists of many nanofibers clusters interwoven into a 3D interconnected network structure, which could largely enhance the overall electrical conductivity of the electrode materials. According to the theoretical calculation, SO_4^{2-} anion shows the highest adsorption energy while the AC^- presents the lowest one (Fig. 10b), displaying that TiN adsorbed by SO_4^{2-} has the most stable structure. More importantly, the capacitance of TiN-based AZICs was positively affected by the structure stability after the anion adsorption. The Zn/TiN capacitor with ZnSO_4 electrolyte demonstrated the highest capacitance (Fig. 10c), which can be ascribed to the more negative adsorption energy of SO_4^{2-} on the TiN cathode and the more stable structure. Besides Zn^{2+} , the SO_4^{2-} anions was significantly involved into the charging/discharging process and consisted the two-step adsorption and intercalation energy storage mechanism (Fig. 10d). Benefiting from the capacitance contribution of SO_4^{2-} and the remarkable electrical conductivity of TiN materials, the device with TiN as cathode and ZnSO_4 as electrolyte presented an ultrahigh capacitance of 489.8 F g^{-1} at 0.2 A g^{-1} and excellent cycling stability over 10,000 cycles (Fig. 10e).

However, metal nitride-based cathodes have not received enough attention in AZICs despite their excellent electrochemical performances derived from the high electrical conductivity and

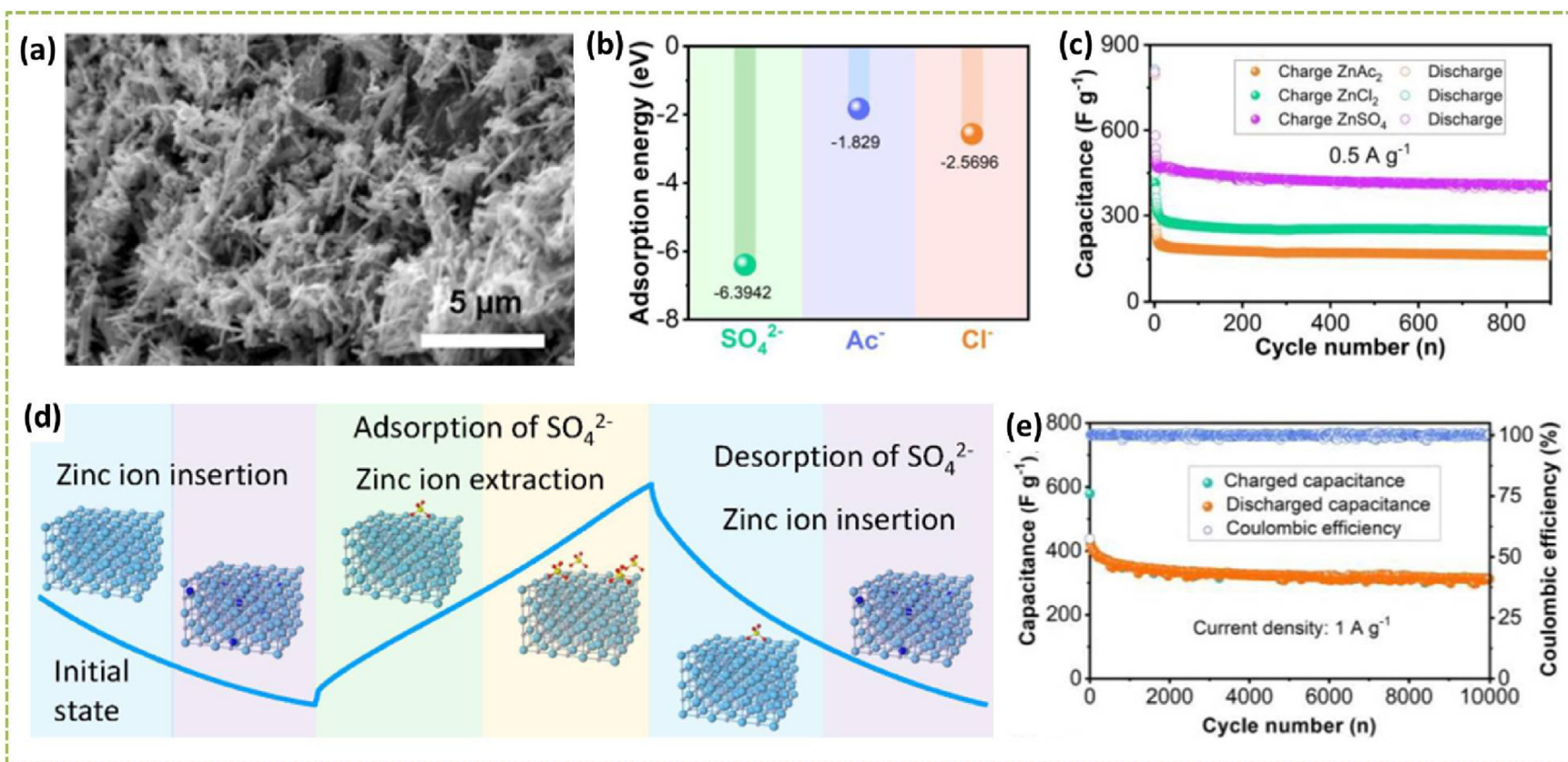


Fig. 10. (a) SEM image of TiN; (b) Comparison of adsorption energy of TiN for different anions; (c) Cycling performance of Zn-TiN capacitor in different electrolyte, respectively; (d) Schematic illustration of the energy storage mechanism during the charging and discharging process and (e) cycling stability at 1 A g⁻¹ of the Zn-TiN capacitor with ZnSO₄ as electrolyte. Reproduced with permission from Ref. [129]. Copyright 2021, Wiley-VCH. (A colour version of this figure can be viewed online.)

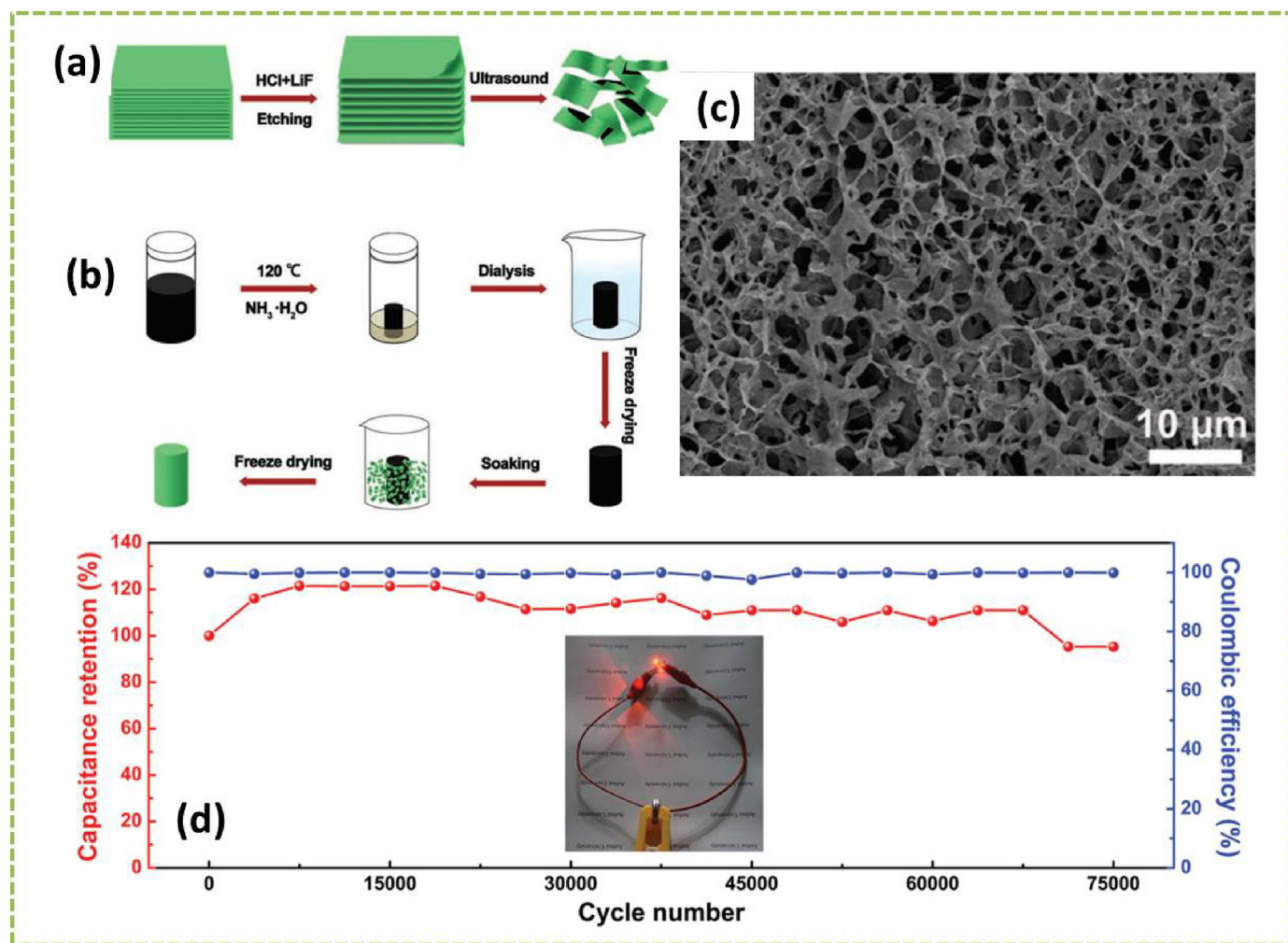


Fig. 11. Illustration of the synthesis procedure of a) MXene nanosheets and b) MXene-rGO aerogels; (c) SEM image of the MXene-rGO aerogel; (d) capacitance retention and coulombic efficiency (The insert exhibits a 1.8 V LED lighted in series) of the MXene-rGO//Zn device. Reproduced with permission from Ref. [135]. Copyright 2019, Wiley-VCH. (A colour version of this figure can be viewed online.)

structural stability. Therefore, we suggest that more efforts should be devoted to developing other metal nitrides.

3.3. MXene

As an analogue of graphene, MXene has a 2D open surface, rich surface chemistry, tunable layer distance, and metallic conductivity, which makes it accommodate/release Zn²⁺ at a high rate and, therefore, could serve as an excellent cathode for AZICs [130–132]. For instance, Yang et al. [133] designed a wholly all-component degradable AZICs using Ti₃C₂ MXene film as the free-standing cathode and Ti₃C₂ film deposited with vertical Zn nanosheets as the anode in an aqueous gel electrolyte. The flexible and free-standing Ti₃C₂ film was prepared by the well-documented acid etching process and vacuum assisted filtration technology. The as-fabricated Zn//MXene capacitor exhibited a good cycling stability (82.5% retention after 1,000 cycles) and a superior rate capability of 91.6% at 3A g⁻¹. More importantly, the device showed an excellent anti-self-discharge performance (6.4 mV h⁻¹) and all the components could be degraded into environmentally benign byproduct within 8 days.

Like other 2D nanomaterials, MXene also faces challenges of surface barriers caused by restacking or aggregation of nanosheets

and poor kinetics because of small interlayer distance [134]. Thus, to overcome these shortcomings, Wang et al. [135] designed a composite of 3D reduced graphene oxide aerogel loaded with MXene (MXene-rGO) and used it as the cathode for AZICs. As demonstrated in Fig. 11a–b, the preparation of MXene-rGO aerogel cathode starts from fabricating the individual components. The synthesis of MXene (Ti₃C₂T_x) includes two typical steps: (1) etching Al layer of bulk MAX Ti₃AlC₂ with the help of HCl and LiF; (2) delamination of multilayer MXene by ultrasound to obtain single-layer nanosheet. On the other hand, 3D rGO aerogel was prepared by hydrothermal GO solution in the presence of ammonia followed by freeze-drying. Then, the final MXene-rGO aerogel products with unique porous structures (Fig. 11c) were recovered by immersing the rGO aerogels into the MXene nanosheets dispersion and freeze-drying, which could be directly used as cathodes without binder and conductive additives. The combination of 3D rGO and MXene could not only effectively prevent the stacking of MXene nanosheets, but also largely improve the electrical conductivity and hydrophilicity of the aerogels. Benefiting from the simultaneous ion adsorption/desorption and intercalation/de-intercalation (fast pseudocapacitive behavior) of MXene-rGO aerogel cathode, AZICs constructed by pairing with Zn anode demonstrated an outstanding performance, especially the extremely long lifespan (75,000 cycles)

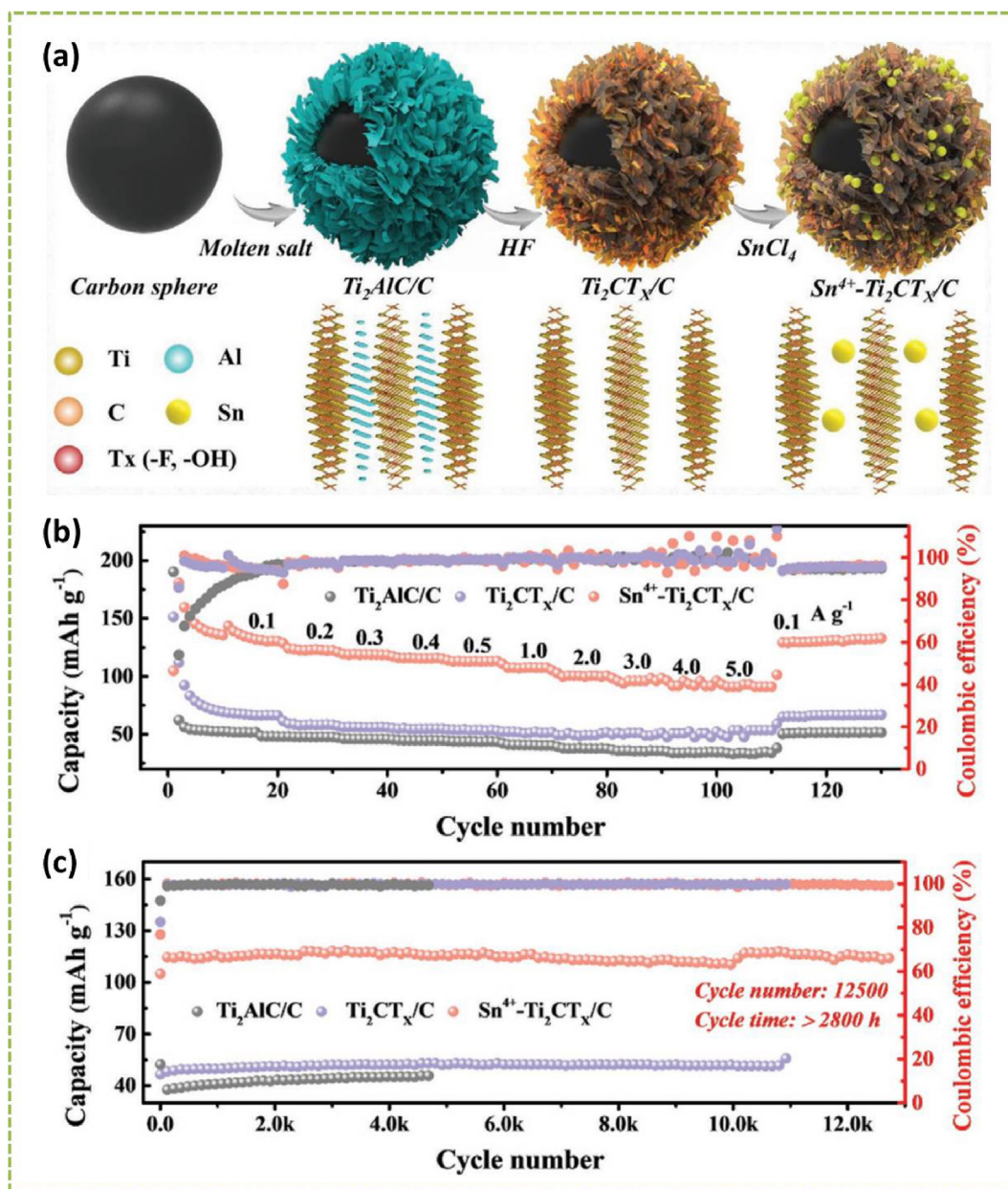


Fig. 12. (a) Schematic illustration of the preparation process of core-shell $\text{Sn}^{4+}\text{-Ti}_2\text{CT}_\text{x}/\text{C}$ sphere; (b) Rate performance and (c) long-term cycling performance at 0.5 A g^{-1} of $\text{Ti}_2\text{AlC}/\text{C}$, $\text{Ti}_2\text{CT}_\text{x}/\text{C}$, and $\text{Sn}^{4+}\text{-Ti}_2\text{CT}_\text{x}/\text{C}$ electrodes. Reproduced with permission from Ref. [136]. Copyright 2020, Wiley-VCH. (A colour version of this figure can be viewed online.)

(Fig. 11d).

Moreover, intercalation into the interlayer of MXene with other ions or compounds is another useful strategy to prevent the restacking of nanosheets. Li et al. [136] designed a pre-intercalated MXene-based cathode to realize high-performance AZICs. The fabrication process has three main steps, as illuminated in Fig. 12a. Firstly, Ti_2AlC MAX was in-situ coated on the surface of carbon spheres by a reaction of Ti, Al and C in a molten salt bath. The Ti_2AlC sheets tightly bond with the carbon sphere surface with strong chemical bonds because of the coating growth mechanism. Then, the Al layers in MAX were selectively etched away by HF solution to obtain $\text{Ti}_2\text{CT}_\text{x}$ MXene. Lastly, $\text{Ti}_2\text{CT}_\text{x}/\text{C}$ was pre-intercalated with Sn^{4+} using SnCl_4 solution as the Sn source to get the final $\text{Sn}^{4+}\text{-Ti}_2\text{CT}_\text{x}/\text{C}$ product. The pre-intercalation of Sn^{4+} effectively enlarged the interlayer spacing of $\text{Ti}_2\text{CT}_\text{x}$ and the aligning of $\text{Ti}_2\text{CT}_\text{x}$ nanosheets on the carbon sphere further improve the ion transportation,

all of which promotes the reaction kinetics. Thus, by paring with Zn anode, the obtained AZICs demonstrated an excellent rate capability of 92 mAh g^{-1} at a high current density of 5 A g^{-1} (Fig. 12b), implying the remarkable improvement of structural design and pillar effect resulting from Sn ion pre-intercalation. Moreover, as shown in Fig. 12c, the device delivered an ultra-long lifespan of 12,500 cycles with only 4% capacity decay, which could be ascribed to the high concentration of electrolyte. Maughan et al. [137] reported a novel in-situ pillared MXene as a reversible and fast Zn^{2+} host where hexadecyltrimethylammonium bromide (CTAB) dissolved in the electrolyte was used to intercalate into the MXene to form a stable interlayer spacing. Compared with the pristine MXene, the intercalation of CTAB enables MXene to present longer cycling life and better rate capability.

AZICs with MXene-based cathodes generally deliver high energy and power density in addition to outstanding cycling stability.

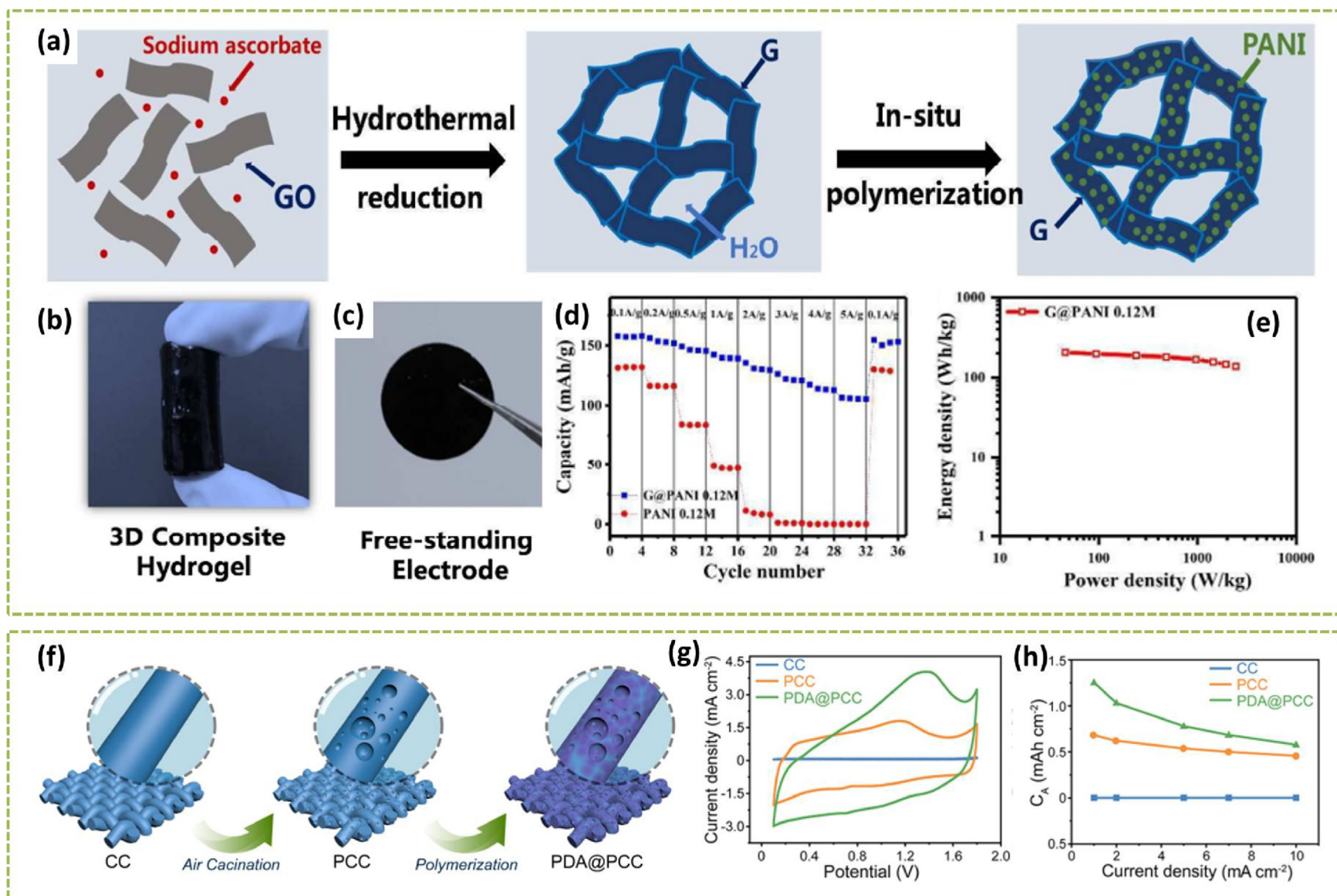


Fig. 13. (a) Illustration for the fabrication process of 3D graphene@PANI hydrogel; the optical images of (b) 3D graphene@PANI hydrogel cylinder and (c) free-standing electrode film; (d) rate capability of PANI electrode and graphene@PANI composite hydrogel electrode; (e) Ragone plot of graphene@PANI-based AZICs. Reproduced with permission from Ref. [144]. Copyright 2018, Royal Society of Chemistry. (f) The schematic preparation process of PDA@PCC; (g) CV curves and (h) rate performance of CC-, PCC-, and PDA@PCC-based AZICs. Reproduced with permission from Ref. [37]. Copyright 2020, American Chemical Society. (A colour version of this figure can be viewed online.)

Nevertheless, the commercial applications of MXene are still hindered by the tedious preparation process using toxic and hazardous reactants. Besides, most MXenes tend to be oxidized when exposed to ambient atmosphere, resulting in structure destruction and conductivity decrease. Furthermore, effective methods to suppress the restacking of MXene layers are also highly demanded. Therefore, these still existing obstacles should be overcome to obtain better MXene-based AZICs.

Generally, transition metal compounds-based cathodes have drawn intensive attention and tremendous progresses have been observed in AZICs. But, in fact, most of these materials fail to reach the expected goal, which are mainly owing to the low electrical conductivity and/or unstable structure, especially for the metal oxides. With this, in order to obtain high-performance electrode materials, it might be much worthy of further exploring new pre-intercalation ions to adjust the interlayer distance and some novel methods to stable the structure. Moreover, surface modification/coating techniques should also be developed to enable the structure stability and to enhance the conductivity of transition metal compounds.

4. Other types of cathode materials

Promoted by their successful applications in MICs and ZIBs, respectively, both the capacitor-type carbon-based materials and the battery-type metal compounds have been well-studied as the cathodes in the current AZICs. Recently, other novel materials have also exhibited exciting electrochemical performance and hold great promise as cathode in AZICs.

4.1. Novel 2D materials

In addition to graphene and MXene, other novel 2D nanostructured materials such as phosphorene and g-C₃N₄ were investigated as cathodes for AZICs. For example, few-layer

phosphorene (FL-P) has attracted intensive attention in energy storage devices due to its large SSA, durable mechanical strength, and high electrical conductivity and carrier mobility, which makes it a potential candidate for AZICs [138–140]. Huang et al. [51] prepared FL-P through the electrochemical exfoliation of black phosphorus and used it as cathode for ZICs. The cathodic delamination method presents an effective and fast way to prepare large and layer-tunable products. The as-prepared FL-P shows a structure of curly ultrathin nanoflakes and these nanosheets tend to form a 3D framework. When pairing with Zn plate anode in a “water in salt” electrolyte, the FL-P-based zinc-ion capacitors demonstrated a high working potential (2.2 V), a high capacitance (304 F g⁻¹ at 0.2 A g⁻¹), an outstanding rate capability (145.9 F g⁻¹ at 6.4 A g⁻¹), and an excellent anti-self-discharge performance. Recently, 2D graphitic carbon nitride (2D g-C₃N₄) was also proposed to be cathode for ZICs [141]. g-C₃N₄ is a photo-active material and can harvest the light due to its band gap in the visible spectrum. Operated in a continuous light powered mode, the photo-rechargeable ZICs using 2D g-C₃N₄ as capacitor-type electrodes present acceptable specific capacity and cycling stability.

4.2. Redox active polymers

Redox-active polymers such as polyaniline (PANI) and polydopamine (PDA) have some unique characteristics including renewability, low cost, flexibility, and have been explored as cathodes in AZICs via interaction of Zn²⁺ with the redox active centers. PANI is a typical pseudocapacitive material for supercapacitors because of its higher specific capacitance compared with other carbon materials-based electrical double layer capacitors [142,143]. However, two main shortcomings impede the commercial applications of PANI. One is its inferior rate capability due to kinetically slow charge transfer reactions and the other one is the poor cycling stability resulted from the mechanical degradation caused by volume change during the charge/discharge process. To overcome

Table 1
Performance comparison of recently reported AZICs with different electrodes.

Cell configuration Anode/Cathode	Voltage (V)	Energy density	Power density	Cycling stability	Ref.
Zn//AC	0.2–1.8	84.0 Wh kg ⁻¹ at 69.0 W kg ⁻¹	14.9 kW kg ⁻¹ at 30.0 Wh kg ⁻¹	91% after 10,000 cycles	[71]
Zn//PSC-A600	0.2–1.8	147.0 Wh kg ⁻¹ at 136.1 W kg ⁻¹	15.7 kW kg ⁻¹ at 65.4 Wh kg ⁻¹	92% after 10,000 cycles	[58]
Zn//HPAC	0.01–1.8	77.5 Wh kg ⁻¹	11.4 kW kg ⁻¹	70% after 18,000 cycles	[43]
Zn//HNPC	0–1.8	107.3 Wh kg ⁻¹	24.9 kW kg ⁻¹	99.7% after 20,000 cycles	[61]
Zn//AC	0.5–1.5	115.4 μWh cm ⁻² at 0.16 mW cm ⁻²	3.9 mW cm ⁻² at 89.0 μWh cm ⁻²	~ 100% after 10,000 cycles	[59]
Zn//3DAC	0.1–1.7	164.0 Wh kg ⁻¹ at 390.0 W kg ⁻¹	9.3 kW kg ⁻¹ at 74.0 Wh kg ⁻¹	90% after 20,000 cycles	[82]
Zn//P&B-AC	0.2–1.8	97.6 Wh kg ⁻¹	12.1 kW kg ⁻¹	88% after 30,000 cycles	[36]
Zn//aMEGO	0–1.9	106.3 Wh kg ⁻¹	31.4 kW kg ⁻¹	93% after 80,000 cycles	[96]
Zn//HPC/CC	0.2–1.8	110.0 Wh kg ⁻¹	20.0 kW kg ⁻¹	100% after 10,000 cycles	[86]
Zn//Ca-900	0–1.8	75.2 Wh kg ⁻¹ at 36.5 W kg ⁻¹	0.88 kW kg ⁻¹ at 43.1 Wh kg ⁻¹	90.9% after 4,000 cycles	[80]
Zn//S-3DPCs	0.2–1.8	162.6 Wh kg ⁻¹ at 160 W kg ⁻¹	16.0 kW kg ⁻¹ at 64.8 Wh kg ⁻¹	96.8% after 18,000 cycles	[108]
Zn//3D graphene@PANI	0.3–1.6	205.0 Wh kg ⁻¹ at 45.8 W kg ⁻¹	2.45 kW kg ⁻¹ at 138 Wh kg ⁻¹	80.5% after 6,000 cycles	[144]
Zn//RGO@PPD	0.2–1.8	1.10 mWh cm ⁻² at 0.8 mW cm ⁻²	8.0 mW cm ⁻² at 0.4 mWh cm ⁻²	100% after 4,000 cycles	[101]
Zn//poly(4,4'-TDP)/AC	0.1–1.9	1.03 mWh cm ⁻²	9.0 mW cm ⁻²	71% after 2,000 cycles	[89]
ACC//Zn _x MnO ₂	0–2.0	969.9 μWh cm ⁻²	20.1 mW cm ⁻²	83.1% after 5,000 cycles	[46]
Ti ₃ C ₂ T _x //MnO ₂ -CNTs	0–1.9	98.6 Wh kg ⁻¹ at 77.5 W kg ⁻¹	2.48 kW kg ⁻¹ at 29.7 Wh kg ⁻¹	83.6% after 15,000 cycles	[45]
Zn//TiN	0.1–1.9	135.0 Wh kg ⁻¹ at 186.0 W kg ⁻¹	3.47 kW kg ⁻¹ at 56.0 Wh kg ⁻¹	~75% after 10,000 cycles	[129]
Zn//RuO ₂ ·H ₂ O	0.4–1.6	119.0 Wh kg ⁻¹	16.74 kW kg ⁻¹ at 82.0 Wh kg ⁻¹	87.5% after 10,000 cycles	[126]
Zn//MXene-rGO	0.2–1.6	34.9 Wh kg ⁻¹	279.9 kW kg ⁻¹	95% after 75,000 cycles	[135]
SM-Zn//AC	0.2–1.8	125.0 Wh kg ⁻¹ at 400.0 W kg ⁻¹	8.0 kW kg ⁻¹ at 20.0 Wh kg ⁻¹	99% after 2,000 cycles	[149]
2D-Zn//AC	0.2–1.8	208.0 Wh kg ⁻¹ at 500.0 W kg ⁻¹	20.0 kW kg ⁻¹ at 66.0 Wh kg ⁻¹	99% after 10,000 cycles	[42]
MCHSs-coated Zn//MCHSs	0.2–1.8	220.1 Wh kg ⁻¹ at 49.8 W kg ⁻¹	11.9 kW kg ⁻¹ at 102.6 Wh kg ⁻¹	100% after 10,000 cycles	[57]
Zn//In//AC	0.2–1.8	70.4 Wh kg ⁻¹ at 85.4 W kg ⁻¹	7.6 kW kg ⁻¹ at 30.2 Wh kg ⁻¹	~ 100% after 5,000 cycles	[150]
(Zn/PC)//PC	0–1.9	104.8 Wh kg ⁻¹ at 58.0 W kg ⁻¹	48.8 kW kg ⁻¹ at 40.4 Wh kg ⁻¹	99.2% after 30,000 cycles	[85]
Zn@CC//OPC	0.2–1.8	82.3 Wh kg ⁻¹ at 41.1 W kg ⁻¹	3.76 kW kg ⁻¹ at 38.6 Wh kg ⁻¹	87.6% after 10,000 cycles	[50]
Zn/C//rGO/CNT	0–1.8	48.5 mWh cm ⁻³ at 179.9 mW cm ⁻³	3598.9 mW cm ⁻³ at 34.0 μWh cm ⁻³	98% after 10,000 cycles	[100]
PAM/PVP coated Zn//AC	0–2.0	118.0 Wh kg ⁻¹	17.9 kW kg ⁻¹	100% after 6,000 cycles	[151]
TiS ₂ //AC	0–1.8	112.0 Wh kg ⁻¹ at 180.0 W kg ⁻¹	3.6 kW kg ⁻¹ at 35.0 Wh kg ⁻¹	92% after 5,000 cycles	[44]



Fig. 14. Illustration of strategies to optimize the performance of AZICs. (A colour version of this figure can be viewed online.)

these drawbacks, forming composite of PANI with nanostructured carbon is a very feasible method. For instance, through a hydrothermal-assisted assembling of GO and chemically in-situ polymerization of aniline, Han et al. [144] developed a pseudocapacitive graphene@PANI composite hydrogel cathode for AZICs. As shown in Fig. 13a–b, 3D interconnected graphene hydrogel was formed by hydrothermally reduction of GO and then aniline was in-situ polymerized on the surface of graphene to produce a self-supporting 3D graphene@PANI composite hydrogel. After cutting into sheet and mechanical pressing, the compressed binder-free hydrogel electrode could be prepared directly (Fig. 13c). The 3D nanostructure can offer more active surface and short diffusion path by increasing the electrode/electrolyte interfaces between the electron transporting phase and ionic transporting phase. In the hybrid cathode, two different Zn^{2+} storage mechanisms exist: adsorption/desorption for graphene (electric double layer capacitance) and redox reaction for PANI (pseudocapacitance). As shown in Fig. 13d, the 3D graphene@PANI cathode-based AZICs showed a high capacity of 154 mAh g^{-1} at 0.1 A g^{-1} and still remain 106 mAh g^{-1} at 5.0 A g^{-1} , exhibiting a much better rate performance than pristine PANI cathode. As expected, the devices delivered an exciting energy density of 205 Wh kg^{-1} (Fig. 13e).

PDA has been investigated as superior cathode and anode materials in batteries because it possesses abundant redox-active carbonyl groups [145–148]. Similarly, it is easy to extend its application in Zn^{2+} -based energy storage devices. Huang et al. [37] developed a free-standing cathode by coating PDA on the porous carbon cloth (PDA@PCC) for AZICs. The preparation process is

demonstrated in Fig. 13f. Carbon cloth was firstly thermally treated at 450°C in air to introduce rich oxygen-containing groups and to increase SSA and, thus, the enhancement of both Zn^{2+} adsorption and PDA loading could be realized. Then, PDA@PCC was successfully obtained by deposited PDA on the PCC through a time-saving hydrothermal polymerization of dopamine. As presented in Fig. 13g, sharply compared with electrochemically inert property of CC and a slight redox peak of PCC, PDA@PCC showed an obvious redox peak which is mainly associated to the reversible reaction between Zn^{2+} and redox-active oxygen-containing groups. Thanks to the adsorption/desorption and fast redox reaction hybrid mechanism, PDA@PCC-based AZICs delivered a higher area capacity (1.25 mAh cm^{-2}) than that of commercial carbon cloth and PCC (Fig. 13h). In addition, no capacity degradation was observed after 10,000 cycles, indicating excellent stability and reversibility.

Based on the reports above, besides porous carbon materials and transition metal compounds, AZICs using 2D nanomaterials and redox active polymers as cathodes also present exciting results. Considering the cost, preparation and electrochemical performance, we suggest that more attention should be paid on redox active polymers. Moreover, polymer-based electrodes have the potential of flexibility that is essential to the wearable devices. However, their rate capability and cycling stability still need to be improved. Therefore, further research could be focused on developing novel polymers with stable structure or fabricating composites with carbon nanofibers, CNTs and graphene.

Overall, significant progresses in cathode materials have been achieved for AZICs, as summarized in Table 1. Obviously, carbon-

based porous materials are still playing a leading role in this realm because of their high performance and easy accessibility. Of course, the recent development of pseudocapacitive cathodes like transition metal compounds and redox active polymers are astounding due to their expected high capacity. However, all these materials still could not fulfill the requirements of high energy density, high power output and long lifespan at the same time, not to mention the commercial expectation. In view of this, it is highly urgent and of significant importance to develop better cathodes for AZICs. As for the carbon-based cathodes, future investigation could focus on improving their capacity by elaborately designing hierarchical porous structure, heteroatom doping and surface modification with functional groups. On the other hand, the structural stability and electrical conductivity of pseudocapacitive cathodes, which greatly influences their cycling life and power density, should be further enhanced by pre-intercalation, surface coating or compositing with other materials.

5. Conclusions and outlook

From this review, it could be easily concluded that AZICs are among the most potential energy storage devices and one of the hottest research topics. By bridging the performance gap between batteries and supercapacitors, AZICs are considered to have very promising applications in many fields, especially those with strong requirements of safety and cost effectiveness. However, the performance of AZICs is still unsatisfactory and their potential has not yet been fully realized despite the recent great progress. Especially, the high energy density could not be obtained at high power density and vice versa due to the low capacity of cathode materials, the narrow operating voltage and the kinetics mismatch of cathode and anode. Given the fact that AZICs is still in the early stage, several aspects should be considered to overcome the challenges faced by the state-of-the-art devices (Fig. 14).

- (1) Developing high-capacity capacitor-type cathode materials. Porous carbons are typical capacitor-type electrode materials to provide high power density and good long-term cycling stability. However, these porous carbons usually have inferior specific capacity because of their adsorption/desorption dominant energy storage mechanism and relatively low electrical conductivity due to serious destruction of structure after activation, leading to unsatisfactory energy and power densities. Doping with heteroatoms and forming composites with redox-active organic small molecules or conductive polymers is an effective strategy to increase the specific capacity of porous carbon by introducing extra pseudocapacitance. Besides, their porosity should be elaborately regulated to obtain high volumetric energy density.
- (2) Designing high-power battery-type cathode materials. Transition metal compounds such as metal oxide are excellent battery-type cathodes and usually deliver higher capacity than porous carbon because of their pseudocapacitive energy storage mechanism. However, this type of cathodes has poor rate and cycling properties which could be ascribed to low electrical conductivity and unstable structure. Coating with conductive materials and pre-intercalating with other ions are effective strategies to tackle these drawbacks. 2D transition metal compounds like MXene are emerging novel cathode materials for their high electrical conductivity, fast intercalation/de-intercalation of zinc ions, and rich surface terminals. Through finely adjusting the layer space of the 2D nanosheets, high gravimetric/volumetric capacity could be obtained simultaneously and, thus, high gravimetric/volumetric energy density could be expected. But the problems

with MXene such as tedious preparation process and oxidation in air need to be addressed.

- (3) As an important part of AZICs, Zn-based anodes suffer from poor rate performance and unstable cycling because of the sluggish redox kinetics, Zn dendrite growth, side reactions, and surface corrosion. To overcome these obstacles, surface engineering, modification and coating are promising strategies to improve the performance of Zn anodes. For example, novel surface structures like nanosheets or nanoneedles could be designed to facilitate ion transport and to enhance rate capability. Surface coating or surface modification with conductive materials need be further investigated. This strategy has great potential in enhancing the stripping/plating efficiency and cycling stability through impeding the Zn corrosion, homogenizing the electric field distribution, and regulating Zn^{2+} flow.
- (4) Better understanding the beneath energy storage mechanism of AZICs. As the development of AZICs is still in its infancy and the electrochemical reactions of multivalent ions are very complicated, the research of electrochemical mechanism is still insufficient and the understanding of some specific mechanism is even controversial. Hence, theoretical calculations and advanced in-situ characterizations are both needed to further understand the energy storage mechanisms of AZICs.
- (5) Constructing flexible AZICs. With the coming of wearable electronics era, the flexible and deformable energy storage devices are highly needed. AZICs featuring high energy density, environmental friendliness and high safety, are the ideal candidates to power wearable smart equipment. Thus, one of the development directions of AZICs is to design flexible and miniature devices with characteristics of repeatedly compressibility/stretchability, biodegradability, biocompatibility and even self-healing function. So, the research pace of flexible electrodes should keep up with this trend. Moreover, gel electrolytes or solid-state electrolytes without leakage risk are preferred to liquid electrolytes.
- (6) Maximizing the working temperature. Currently, the operational temperature of AZICs is mainly limited by the electrolytes. Especially, the freeze of the aqueous electrolyte restricts their low temperature application. One possible solution is through modulating the electrolyte structure to break the hydrogen-bond network and thus to suppress the solid-liquid transition temperature of aqueous electrolyte. Developing mixture solvents (such as adding organic solvents or ionic liquids to aqueous electrolytes to form eutectic system) might provide another promising solution.
- (7) Achieving wider operation voltage. The improvement of energy density of AZICs is hindered by the relatively low working voltage (typically lower than 2 V) due to the decomposition of water. Water-in-salt electrolytes keeps the advantages of non-flammability and environmental friendliness as the conventional dilute aqueous electrolytes but show wider stability window by reducing the electrochemical activity of the electrolyte through minimizing the amount of free water molecules, thereby providing a strategy to widen the potential window of AZICs. Furthermore, to achieve higher voltage, developing novel electrolyte additives and tuning the electrolyte composition are also desired strategies.

In summary, AZICs are among one of the most appealing energy storage technologies and have gained tremendous progresses despite still remaining challenges. We believe that the rational design of high-performance cathode and anode materials will

greatly promote the commercial applications of AZICs.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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