Recent progress and future prospects of sodium-ion capacitors

Rui Jia¹, Guozhen Shen^{2*} and Di Chen^{1*}

ABSTRACT To satisfy the requirements for various electric systems and energy storage devices with both high energy density and power density as well as long lifespan, sodium-ion capacitors (SICs) consisting of battery anode and supercapacitor cathode, have attracted much attention due to the abundant resources and low cost of sodium source. SICs bridge the gap between the batteries and the supercapacitors, which can be used as competitive candidates for large-scale energy storage. In this review, the battery-type anode materials and the capacitor-type cathode materials are classified and introduced in detail. The advantages of various electrolytes including organic electrolytes, aqueous electrolytes and ion liquid electrolytes are also discussed sequentially. In addition, from the perspective of practical value, the presentations of the SICs at the current situation and the potential application in urban rail are displayed. Finally, the challenge, future research and prospects towards the SICs are put forward.

Keywords: sodium-ion, hybrid capacitors, battery-type anode, capacitor-type cathode, electrolytes

INTRODUCTION

With the increasing consumption of traditional fossil fuels and growing serious environment pollution, the development of clean energy (such as wind energy and solar power) and efficient energy storage systems (ESS) has become more and more important [1–9]. Commercial lithium ion batteries (LIBs) possessing high energy density (150–200 W h kg^{−1}) are restricted by low power density (less than 350 W kg^{−1}). Meanwhile, supercapacitors (SCs) owning high power density (~10 kW kg^{−1}) are limited by low energy density (no more than 10 W h kg^{−1}) [10,11]. In the past decades, many efforts have been made to boost the power and energy densities of the batteries and capacitors, respec-

tively. For instance, with the advent of electric vehicles (EVs), which require long lifespan (> 10 years) and a high power density (> 1000 W kg^{−1}), lithium-ion hybrid capacitors (LICs) combining the features of high energy and high power densities were developed [12–19]. Compared with SCs and LIBs, LICs combine the advantages of the above two types of energy storage devices. However, the element of lithium on earth is not rich and geographically limited in the worldwide, resulting in the price of lithium skyrocketing with the appearance of EVs. The high cost restricts the large-scale application of LICs in ESS. On the other hand, sodium (Na) has similar chemical properties to Li and abundant resource (2.75% of Na to 0.065% of Li on earth) [20]. Additionally, sodium does not react with aluminum, which makes it possible to replace the expensive copper current collector. Consequently, sodium ion capacitors (SICs) have attracted much attention since 2012 [21–25].

The charge storage mechanism of hybrid capacitor is based on reversible anion adsorption/desorption on the surface of the cathode and Na-ion reversible intercalation/de-intercalation in the anode [5,7]. The SICs generally exhibit higher energy densities from the Faradic reactions of battery-type anode than SCs and higher power densities from the capacitive reaction on the cathode than the batteries. Although SICs can bridge the gap between SCs and batteries, the energy and power densities of SICs are still dissatisfying by the requirements of large-scale ESS at present. The reason is that the radius of Na-ion (1.02 Å) is larger than that of Li-ion (0.76 Å), which results in sluggish Na-ion diffusion and subversive structure changes in electrode materials during the charge and discharge process and reduces the rate capacity and cycling properties [26]. That is to say, SICs devices are in the primary stage of development and still face myriad problems from the electrode materials, electrolytes and

¹ School of Mathematics and Physics, University of Science and Technology Beijing, Beijing 100083, China

² State Key Laboratory for Superlattices and Microstructures, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, China

* Corresponding authors (emails: chendidi@ustb.edu.cn (Chen D); gzshen@semi.ac.cn (Shen G))

practical applications. Nonetheless, the late beginning also means more opportunities and progress should be achieved *via* solving the complicated questions.

In this review, we summarize the recent progress of SIC devices, which is disserted as following: (1) electrode materials including anode materials (carbon materials, transition metal oxides and compounds, transition metal chalcogenides and nitrides, MXenes, sodium super ion conductor (NASICON) materials and alloys) and cathode materials (porous carbon materials, MXenes and Prussian blue (PB) materials), (2) electrolyte (aqueous, organic and ionic liquid electrolytes), (3) presentation and potential application of the SICs. At the end of the review, we discuss the emerging questions in SICs and put forward our suggestions in responds to the existing problems for the future perspectives.

STRATEGIES TOWARD ELECTRODE MATERIALS OF SICs

The electrode materials play a very important role in the electrochemical properties of SICs. The anode materials of SICs as Na-ion hosts should have expanded lattice spacing, improved surface-controlled pseudocapacitance and reduced diffusion distance to enhance the kinetic behaviors. For example, the carbon materials with heteroatom doping, transition metal oxides and compounds, transition metal chalcogenides and nitrides, MXenes, NASICON and alloys are often involved. As for the cathodes, the materials with the features of high specific surface area and good electrical conductivity are necessary, such as porous carbon, MXenes and PB. In the following part, the developments on the anode and cathode materials during the past several years are described in details.

Battery-type anode materials

Carbon materials

Carbon materials are regarded as promising candidates for Na-ion storage, due to their abundance in reserve, excellent electrical conductivity, high chemical stability and adjustable structure [27–34]. Most studies have focused on disordered carbon with large interlayer distance and numerous voids, which are beneficial to Na-ion insertion/extraction. In addition, some reports also involved the ordered carbon with uniform pore structures, which can contribute to facilitating the ion diffusion. In the early stage of SICs research, the sodium pre-doped hard carbon//activated carbon (AC) device fabricated by Kuratani and co-workers [35] in 2012 was the first report

confirming that the sodium pre-doped hard carbon can stand a high current density applicable to capacitors. However, the SICs with the reported hard carbon as anode materials possess a low capacity and voltage, which needs to be further enhanced [36–38]. Graphite as the typical anode material in Li-based ESS is not suitable for Na-ion intercalation because of unfavorable mismatch between the size of Na-ion and the well-ordered structure [39]. Fortunately, in 2015, Han *et al.* [40] introduced Na⁺-diglyme co-intercalation method, realizing the reversible Na-ion insertion into graphite. The decent energy and power densities of 93.5 W h kg⁻¹ and 2823 W kg⁻¹ in the potential window of 1–4 V were obtained from the graphitic mesocarbon microbead (MCMB)//AC device. Even after 3000 cycles, the capacitance retention still remains 98.3%, suggesting a good cycling performance of MCMB//AC based SICs. Moreover, the reduced graphene oxide (rGO) has also been used as anode, in which the Na⁺ can intercalate by reduction of C=O groups to –O–Na or be stored by noncovalent interaction between the rGO layers. The rGO//Na_{0.21}MnO₂ based SIC [41] in Na₂SO₄ aqueous electrolyte with the voltage of 2.7 V shows high energy density of 31.8 W h kg⁻¹ and high power density of 8000 W kg⁻¹. After 1000 cycles, the capacitance remained 86.7% of the initial value without water splitting.

Designing porous carbon materials with two dimensional (2D)/3D structure and introducing heteroatom (N, O, S, P) into the carbon network can improve the energy storage performance [29]. In general, the 2D or 3D porous structure can enhance the rapid transportation, migration and diffusion of sodium ions and supply abundant active sites for reactions. Furthermore, the incorporation of heteroatoms can not only provide extra defects, but also contribute to redox reactions, which can facilitate the sodium ion storage. In 2017, sodium storage device based on graphdiyne nanosheets (GDY-NS) electrodes with good electronic conductivity and mechanical properties was designed for the first time by Wang and co-workers [42], as shown in Fig. 1a and b. Notably, the fabricated GDY-NS//AC based SICs illustrated excellent rate performance and long cycling lifespan, in which the capacitance still retained >90% after 3000 cycles (Fig. 1c and d). The SICs delivered an energy density of 182.3 W h kg⁻¹ at the power density of 300 W kg⁻¹ and 166 W h kg⁻¹ at 15,000 W kg⁻¹, which were much higher than that of carbon nanosheets//carbon nanosheets based devices [43]. The layered structure with intramolecular pores of GDY-NS electrode can greatly increase the active sites and promote the fast ion transfer for sodium-ion

Figure 1 (a) Schematic diagram of the sodium-ion diffusion and sodiation in GDY-NS materials. (b) Top view SEM image of GDY-NS on the Cu substrate. (c) Rate performance of the GDY-NS//AC SICs at various current densities from 50 mA g⁻¹ to 5 A g⁻¹. (d) The cycling performance of the GDY-NS//AC SICs at the current density of 1 A g⁻¹. Reproduced with permission from [42]. Copyright 2017, American Chemical Society. (e) Schematic illustration of the preparation of EDHPC and the fabrication of EDHPC//EDHPC SICs. (f, g) XPS survey spectrum and XRD pattern of EDHPC. (h, i) Charge-discharge curves of two half cells and the EDHPC//EDHPC SICs. (j) Ragone plots of SICs. Reproduced with permission from [44]. Copyright 2018, Springer.

storage. Recently, Liu and co-workers [44] fabricated the symmetric SICs based on enteromorpha-derived hierarchical porous carbon (EDHPC) electrode materials with a 3D sponge-like network structure through simultaneous activation and carbonization process as shown in Fig. 1e. The X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) results show that besides carbon, some other elements including N, O and S also coexist in EDHPC electrode with the disordered structure (Fig. 1f and g). The presence of heteroatoms in EDHPC can be

involved in surface redox reactions and introduce extra active and defective sites for additional charge accumulation. Encouragingly, the assembled SICs with the extended potential window of 0–4 V obtain the maximum energy density of 84 W h kg⁻¹ and power density of 9053 W kg⁻¹ as displayed in Fig. 1h–j. The EDHPC electrodes have the advantages of large specific surface area (1968 m² g⁻¹), hierarchical porosity and heteroatom doping, which are beneficial to improving the electrochemical performance.

Transition metal oxides and compounds

Besides carbon materials, many transition metal oxides such as V_2O_5 , MnO_2 , Fe_3O_4 , MoO_2 , Nb_2O_5 and TiO_2 [45,56] with constructed nanostructures have been explored as pseudocapacitive anode materials, in which the distinctive microstructures with sizable tunnels can reduce the diffusion pathways of the ions. As reported, the layer-structured V_2O_5 with large lattice distance of 9.5 Å ((001) plane) has miscellaneous oxidation states, demonstrating obvious pseudocapacitive behavior. Nevertheless, the low electrical conductivity ($\sim 10^{-6} \text{ S cm}^{-1}$) limited the applications of V_2O_5 for high-performance SICs. In order to improve the electric conductivity of the electrode materials, constructing transition metal oxide composites with carbon materials is one of the most common approaches. For example, in 2012, Chen *et al.* [45] fabricated a SIC device using V_2O_5 /carbon nanotube (CNT) nanocomposite synthesized through one-pot hydrothermal process as anode and AC as cathode in 1 mol L^{-1} $NaClO_4$ organic electrolyte, which gave a maximum energy density of 38 $W h kg^{-1}$ at a power density of 140 $W kg^{-1}$ and a high power density of 5000 $W kg^{-1}$ at an energy density of 7.5 $W h kg^{-1}$, respectively. In this work, the CNTs can link the small V_2O_5 crystal domains and supply enhanced electronic conductivity, leading to an increased rate of charge transfer. In addition, Nb_2O_5 has been recognized as a promising anode material for LIBs due to its dominating pseudocapacitive properties and the large interlayer lattice spacing of 3.9 Å ((001) plane). The self-assembled Nb_2O_5 NSs cluster anode and peanut shell carbon (PSC) cathode were used to fabricate SICs, which exhibited a high energy density (43.2 $W h kg^{-1}$), high power density (5760 $W kg^{-1}$) and a capacity retention of 80% after 3000 cycles [50]. Carbon material composited Nb_2O_5 electrodes can significantly improve the electrochemical performance of SICs. For example, in 2016, Lim *et al.* [51] presented a sodium-ion hybrid SCs using Nb_2O_5 @carbon core-shell nanoparticles combining with rGO nanocomposites as anode and MSP-20 as cathode, which delivered high energy/power density (76 $W h kg^{-1}$ and 20,800 $W kg^{-1}$) in the voltage of 1.0–4.3 V. Recently, Wang and co-workers [52] prepared typical composited electrodes through directly growing ultrathin graphene shells over T- Nb_2O_5 nanowires (Gr- Nb_2O_5) by plasma enhanced chemical vapor deposition (PECVD) as displayed in Fig. 2a and b. The synergistic effect between Nb_2O_5 nanowires and graphene shells has merits of shortening ion diffusion path and enhancing electronic conductivity of electrode. As a result, 61.2% of the total

capacity of the Gr- Nb_2O_5 electrode originated from surface capacitive effect at a small scan rate of 0.5 $mV s^{-1}$. Fig. 2c further shows that $\sim 67 W h kg^{-1}$ of the energy density and above 97.1% of Coulombic efficiency can be maintained at 1 $A g^{-1}$ after 1500 cycles, demonstrating that the SICs own a stable cycling performance. Meanwhile, the SIC devices of Gr- Nb_2O_5 //AC delivered the maximum energy density of $\sim 112.9 W h kg^{-1}$ and the high power density of $\sim 5330 W kg^{-1}$ as shown in the inset of Fig. 2c. The unique core/shell structure of Gr- Nb_2O_5 is beneficial to the electron and Na^+ transport, guaranteeing rapid pseudocapacitive reactions on the interface of Nb_2O_5 and electrolyte. In brief, the methods of combining with carbon materials and constructing special nanostructures can effectively improve sodium ion energy storage.

Ti-based oxides with low volume expansion and low voltage can be considered as hopeful anode materials for sodium-ion storage. Similarly, poor electron conductivity of the bulk TiO_2 hinders its usage. As a consequence, many efforts have been made to improve the conductivity of the Ti-based oxides. For example, in 2017, Le *et al.* [54] synthesized single-crystal-like TiO_2 anchored on graphene by microwave-assisted solvothermal method. In sodium ions half cells, around 73% of the capacity can be ascribed to the capacitive contributions at the scan rate of 3 $mV s^{-1}$. The SICs connecting AC cathode show a high energy density of 64.2 $W h kg^{-1}$ and high power density of 1357 $W kg^{-1}$, as well as 90% of capacitance retention after 10,000 cycles. Meanwhile, another novel SICs using TiO_2 @CNT@C nanorods as anode and biomass-derived carbon as cathode were fabricated in 2017 [55]. According to scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HRTEM) images (Fig. 2d and e), TiO_2 nanomaterials and multi-wall CNTs (MWCNTs) both exist in carbon nanorods. The maximum value of the capacitive contribution is 81% at the scan rate of 3 $mV s^{-1}$ for the TiO_2 @CNT@C, indicating that a large proportion of the capacity originates from the surface-controlled pseudocapacitance. Due to the improved electrical conductivity in the presence of MWCNTs, the SICs can obtain an exceptionally high energy and power densities of 81.2 $W h kg^{-1}$ and 12,400 $W kg^{-1}$ in the potential window of 1.0–4.0 V as displayed in the Fig. 2f. Moreover, the fabricated SICs achieve 85.3% of the capacitance retention after 5000 cycles. This work offers a method to improve the conductivity of the TiO_2 by incorporating MWCNTs. Besides the approach of making composites with conductive materials, narrowing the band gap of the electrodes can

Figure 2 (a) Schematic illustration of Gr-Nb₂O₅ composites. (b) SEM image of Gr-Nb₂O₅ composites. (c) The long-term cycling performance of the Gr-Nb₂O₅//AC SICs at 1 A g⁻¹. The inset shows the rate capability of the SICs at various current densities from 0.03 to 2 A g⁻¹. Reproduced with permission from [52]. Copyright 2018, Wiley-VCH. (d, e) SEM and HRTEM images of TiO₂@CNT@C. (f) Charge-discharge curves of TiO₂@CNT@C//BAC SICs at various current densities in the potential of 1–4 V. Reproduced with permission from [55]. Copyright 2017, Wiley-VCH. (g) Field emission SEM (FESEM) image of NTO/ACF nanocomposite. (h) Cyclic voltammetry (CV) curves of the ACF//NTO/ACF SICs at different current densities. (i) Ragone plots compared with other reports. Reproduced with permission from [63]. Copyright 2018, Royal Society of Chemistry.

also remarkably improve the electric conductivity. In 2018, Babu *et al.* [56] reported semicrystalline brown TiO₂ nanotubes (BTNT) with Ti³⁺ by a hydrothermal route, which can enhance conductivity through shortening the colossal band gap. Through the kinetics studies, 57% of the total charge was surface capacitive contribution in the BTNT electrode at a scan rate of 1 mV s⁻¹, which was higher than crystalline dark brown TiO₂ (47%) in the same work. And the fabricated BTNT//AC device achieved a maximum energy density about 68 W h kg⁻¹, a high power density around 12,500 W kg⁻¹ and a good cycling performance with 80% capacitance retention up to 10,000 cycles.

Na₂Ti₃O₇ (NTO), one kind of Ti-based compound, has recently been extensively explored owing to its rich reserves, low toxicity and high theoretical capacity of

310 mA h g⁻¹. In particular, NTO possesses the lowest voltage (0.3 V vs. Na⁺/Na), demonstrating that it can be a promising candidate as anode material for SICs [57–61]. For example, in 2016, Li and co-workers [62] reported a quasi-solid-state SIC with urchin-like NTO as anode prepared by hydrothermal reaction and peanut shell derived carbon as cathode, using Na⁺ ions conducting gel polymer as electrolyte. The high energy and power densities can reach 111.2 W h kg⁻¹ and 11,200 W kg⁻¹, respectively. Recently, Qiu *et al.* [63] reported the *in situ* fabrication of NTO NSs on the AC fiber (ACF) through electrospinning, one-pot carbonization, activation and subsequently the hydrothermal process (Fig. 2g). The electrochemical measurements of the SICs were performed in the potential range of 0–3 V (Fig. 2h and i). The Ragone plots of SICs based on NTO/ACF//ACF

electrodes showed a high energy density of $127.73 \text{ W h kg}^{-1}$ at the power density of 95.79 W kg^{-1} , higher than that of ACF//NTO and other SCs based on NTO electrodes [58,60,62,64]. The surface-controlled capacitance ratio of NTO/ACF nanocomposites was higher than that of the pure NTO at the same scan rates because of the electric double layer capacitor behavior of the ACF. With the aid of ACF, the transportation and diffusion of Na^+ can be enhanced. Simultaneously, the structural stability and electronic conductivity of the electrode materials would also be highly improved. In addition, spinel NiCo_2O_4 was involved in SICs as anode material and exhibited good electrochemical performance. Yang *et al.* [65] prepared the SICs device by employing pre-sodiated NiCo_2O_4 as anode and AC as cathode. During the reaction, the pre-sodiated NiCo_2O_4 electrodes converted to Na_2O , metallic Ni and Co, which were kinetically beneficial to fast interfacial electrochemical reactions. The SICs delivered the maximum energy and power densities of $120.3 \text{ W h kg}^{-1}$ and $10,000 \text{ W kg}^{-1}$, respectively, which were 5–9 times higher than other SICs based on NiCo_2O_4 without pre-sodiation [66].

Transition metal chalcogenides and nitrides

Transition metal sulfides (MoS_2 and SnS_2) with layered structure and large interplanar distance have been applied in energy storage devices in recent years [67–70]. However, the poor inherent electronic conductivity causes serious polarization and low electrode utilization efficiency. Consequently, optimizing the nanostructure and enhancing the conductivity of the transition metal sulfides are vital and effective to achieve high pseudocapacitive charge storage. For example, the layered SnS_2 has a large interlayer spacing of 0.59 nm in favor of the insertion/extraction of Na^+ . In 2016, Chauhan *et al.* [68] synthesized SnS_2 /RGO NSs under *in situ* hydrothermal conditions. The fabricated symmetric SnS_2 /RGO// SnS_2 /RGO hybrid capacitor in Na_2SO_4 solution exhibited a specific capacitance of 500 F g^{-1} , energy density of $16.67 \text{ W h kg}^{-1}$ and power density of 488 W kg^{-1} . The 2D layered structure, enhanced electron mobility and synergistic effect of graphene sheets with SnS_2 NSs led to good energy storage performance of the electrode material. Similar to SnS_2 , in 2017, Wang *et al.* [69] prepared monolayer MoS_2 -carbon (MoS_2 -C) composites with expanded interlayer spacing from 0.62 to 0.98 nm through atomic interface modification method. The pseudocapacitive contribution ratio of the MoS_2 -C electrode was 76.7% at 5 mV s^{-1} . More importantly, the SICs were

prepared with MoS_2 -C as anode and polyaniline derived porous carbon (PDPC) as cathode in $1 \text{ mol L}^{-1} \text{ NaClO}_4$ electrolyte, which can get a maximum energy density of $111.4 \text{ W h kg}^{-1}$, a high power density of $12,000 \text{ W kg}^{-1}$ and a good capacitance retention of 77.3% for 10,000 cycles. Zhao and co-workers [70] also reported an enhanced sodium storage capability enabled by MoS_2 supported on carbon fibers (E- MoS_2 /carbon fibers) with a wide interlayer spacing of 1.34 nm (Fig. 3a and b), which was almost twice as large as that of the commercial MoS_2 in 2017. In addition, the structural model of the E- MoS_2 /carbon fibers in Fig. 3c was in accordance with the HRTEM result. At the scan rate of 2 mV s^{-1} , the capacitive contribution can reach up to 89.4% . Based on E- MoS_2 /carbon fibers as anode and commercial AC as cathode, the SICs can operate under the potential range from 1.0 to 4.3 V in $1 \text{ mol L}^{-1} \text{ NaClO}_4$ electrolyte and deliver the high energy density of 54.9 W h kg^{-1} as shown in Fig. 3d. The special structure of E- MoS_2 /carbon fibers with the features of shortened ion diffusion pathways, enhanced electron transfer and easily accessible active sites was conducive to improving the capacitive contribution of the electrode materials and the electrochemical performance of SICs.

As an analogue to transition metal sulfides, transition metal selenides have also attracted research attention in SICs. For example, MoSe_2 with the features of layered structure, large interlayer distance (0.64 nm), narrow band gap (1.1 eV) and high theoretical capacity (422 mA h g^{-1}) stands out from various candidates [71]. However, the issues of intrinsic inferior electronic conductivity and big volume change hinder the usage of MoSe_2 . To solve these problems, Zhao *et al.* [72] designed ordered MoSe_2 /graphene nanocomposite through hydrothermal method in 2018. The MoSe_2 NSs can produce enough open space to accommodate the volume changes during Na-ion insertion/extraction. Furthermore, the graphene not only improved the electrical conductivity of the materials, but also kept the MoSe_2 NSs from aggregation. Meanwhile, the Mo–C chemical bonding can significantly enhance the charge transfer in the electrode material. The assembled MoSe_2 /graphene//AC SICs showed good cycling stability at 5 A g^{-1} for 5000 cycles with a high energy and power density of 82 W h kg^{-1} and $10,752 \text{ W kg}^{-1}$, respectively. Similarly, a method of *in situ* growing CoSe_2 @vertically-oriented graphene hierarchical architecture on carbon cloth (CoSe_2 @VG/CC) through PECVD and wet chemistry was reported by Xia and co-workers in 2019 [73]. This electrode with superstructure can be prepared without binders/additives and beneficial

Figure 3 (a, b) SEM and HRTEM images of the E-MoS₂/carbon fibers. (c) Structural models of the MoS₂ with different interlayer spacings. (d) GCD curves of the E-MoS₂/carbon fibers//AC SICs at various current densities. Reproduced with permission from [70]. Copyright 2017, Elsevier. (e) GCD curves of the VN-MWCNT//MnO₂-MWCNT SICs at different currents. (f) Ragone plot of the hybrid SICs. The insets display the VN-MWCNT//MnO₂-MWCNT coin cell that used for tests and powering LED bulbs. Reproduced with permission from [75]. Copyright 2014, Elsevier. (g) Schematic of the synthesis process for Ti(O,N)-MP-NWs. (h) Elemental mapping images of Ti(O,N)-700. (i) The cycling performance of the Ti(O,N)//AC SICs. (j) Ragone plots of various supercapacitors. Reproduced with permission from [76]. Copyright 2017, Royal Society of Chemistry.

to fast electron/ion diffusion. The fabricated CoSe₂@VG/CC//AC SICs delivered a high energy and power density of 116 W h kg⁻¹ and 7298 W kg⁻¹, respectively.

Due to superior electronic conductivity and high pseudocapacitance, the transition metal nitrides are considered as promising electrodes, especially, the VN and TiN [74–76]. For example, in 2015, Su and co-workers [75] developed a hybrid SC with VN-MWCNT negative electrode and MnO₂-MWCNT positive electrode in Na₂SO₄ electrolyte, operated under the potential of 0–1.8 V as displayed in the Fig. 3e. The galvanostatic charge/discharge (GCD) curves displayed nearly triangle shape with good Coulombic efficiency. Meanwhile, the

potential drops were not obvious at low currents, demonstrating that the internal resistance of the device was very low. After 1000 cycles, the capacitance retention retained 80%, suggesting a good cycling performance of the SICs. Fig. 3f exhibited the maximum energy and power densities of 38.7 W h kg⁻¹ (19.4 mW h cm⁻³) and 316.2 W kg⁻¹ (158.1 mW cm⁻³), respectively. Inset of Fig. 3f shows that three light-emitting diode (LED) bulbs can be simultaneously lighted by VN-MWCNT//MnO₂-MWCNT coin cells. Furthermore, in 2017, Dong *et al.* [76] synthesized titanium oxynitride mesoporous nanowires (Ti(O,N)-MP-NWs) with tunable O/N ratios based on an anion exchange process in Fig. 3g. A large number

of holes occurred in the whole course that can be beneficial to contact with the NaClO_4 organic electrolyte. The capacitive contribution of the $\text{Ti}(\text{O},\text{N})$ -700 in sodium ion half cell was about 78.9% at 2 mV s^{-1} . Elemental mappings in Fig. 3h states that the sample consists of Ti, N and O. Before assembling SICs device, the $\text{Ti}(\text{O},\text{N})$ -MP-NWs were pre-sodiated for two cycles. Fig. 3i shows the charge/discharge curves of the SICs in the voltage of 0.5–4 V, achieving a specific capacity of 56 C g^{-1} at 1 A g^{-1} . The maximum energy and power densities of the $\text{Ti}(\text{O},\text{N})$ -MP-NWs//AC device were 46 W h kg^{-1} and $11,500 \text{ W kg}^{-1}$ (Fig. 3j), higher than that of previously reported similar SIC devices including TiN//TiN , AC//TiO_2 -rGO, $\text{TiN@GNS//Fe}_2\text{N@GNS}$, CNT//TiO_2 (B), and AC//TiO_2 (anatase) [5,77–79]. The features of excellent conductive nature, largely increased surface reaction sites and short ion diffusion pathways of the $\text{Ti}(\text{O},\text{N})$ -MP-NWs demonstrate the $\text{Ti}(\text{O},\text{N})$ -MP-NWs can be prospectively used as the electrode in SICs.

MXenes

2D MXenes discovered in 2011 are a hot issue with few-atom layered structures that can be reversibly inserted/extracted with foreign cations as anode materials in SICs. The formula of MXenes is $\text{M}_{n+1}\text{X}_n\text{T}_m$, where M represents the transition metal (Ti, V, Nb, Ta, Cr, Mo), X is C and/or

N, T is the surface function group ($-\text{OH}$, $-\text{F}$, $-\text{O}$), and $n = 1, 2$ or 3 [80]. In the past few years, many studies referred to MXenes as anode materials in SICs due to the expanded d -spacing through selectively etching and further activation processes. For example, in 2014, Wang *et al.* [81] synthesized Ti_2CT_x with expanded interlayer distance of $7.7 \text{ \AA}$ (initial value of $6.8 \text{ \AA}$) via etching in HF aqueous solution. Then, the intercalation of Na^+ in the Ti_2CT_x sheets resulted in the interlayer distance further enlarging to $10.1 \text{ \AA}$ by the first cathodic reaction (Fig. 4a). The d -spacing can keep unchanged in the following charge/discharge process, illustrating that the reaction mechanism was based on pseudocapacitance. In addition, HRTEM results also confirmed the change of d -spacing in Ti_2CT_x after reactions (Fig. 4b and c). The prepared $\text{Ti}_2\text{CT}_x/\text{Na}_2\text{Fe}_2(\text{SO}_4)_3$ SIC devices showed extremely stable efficiency and cycling properties after the initial cycles, ascribed to the pseudocapacitance behavior of the MXene material as shown in Fig. 4d. A high energy density of 260 W h kg^{-1} at high specific power density of 1400 W kg^{-1} can be obtained based on the weight of Ti_2CT_x . Furthermore, the prepared $\text{Ti}_3\text{C}_2\text{T}_x$ using *in situ* HF formation etchants (LiF and HCl) has high electrical conductivity, large flake sizes, environmental stability and good mechanical properties. In 2016, Xie *et al.* [80] mixed the $\text{Ti}_3\text{C}_2\text{T}_x$ (negatively charged) and the CNTs (positively

Figure 4 (a) Schematic illustration of the reaction mechanism of Ti_2CT_x by electrochemical activation. (b, c) TEM images of the pristine Ti_2CT_x and activated Ti_2CT_x after the first cycle. (d) The cycling stability and Coulombic efficiency of the $\text{Ti}_2\text{CT}_x/\text{Na}_2\text{Fe}_2(\text{SO}_4)_3$ SICs in the voltage of 0.1–3.8 V. Reproduced with permission from [81]. Copyright 2015, Macmillan Publishers Limited. (e) Schematic diagram of the self-assembly preparation of $\text{Ti}_3\text{C}_2\text{T}_x/\text{CNT}$. (f) Cross-section SEM image of porous $\text{Ti}_3\text{C}_2\text{T}_x/\text{CNT}$. Reproduced with permission from [80]. Copyright 2016, Elsevier.

charged) to prepare porous self-assembled $\text{Ti}_3\text{C}_2\text{T}_x/\text{CNT}$ ($\text{Ti}_3\text{C}_2\text{T}_x/\text{CNT-SA}$) by electrostatic interaction, in which the interspersed CNTs can significantly avert the MXene NSs restacking in Fig. 4e and f. More importantly, the d -spacing of the $\text{Ti}_3\text{C}_2\text{T}_x/\text{CNT-SA}$ was 16.4 Å calculated from the XRD diffraction peak location, supplying channels for Na ions transport. Meanwhile, compared with the initial $\text{Ti}_3\text{C}_2\text{T}_x$ ($19.6 \text{ m}^2 \text{ g}^{-1}$), the $\text{Ti}_3\text{C}_2\text{T}_x/\text{CNT-SA}$ composites had increased specific surface area of $185.4 \text{ m}^2 \text{ g}^{-1}$ with much more active sites for electrochemical reactions. According to the kinetics calculation, the non-diffusion limited current was 88.1% of the whole charge at the scan rate of 0.1 mV s^{-1} , demonstrating that the open structure of the $\text{Ti}_3\text{C}_2\text{T}_x/\text{CNT-SA}$ was beneficial to electrolyte diffusion. For the SICs assembled based on $\text{Ti}_3\text{C}_2\text{T}_x/\text{CNT-SA}$ anode and $\text{Na}_{0.44}\text{MnO}_2$ cathode, the first and 60th discharge capacities were 286 and 242 mA cm^{-3} at the current density of 50 mA g^{-1} , respectively, indicating a relatively stable cycling performance of the devices. This study provides a simple and efficient strategy to enhance the accessibility of MXenes to liquids or gases, which is expected to facilitate the applications of the MXenes in batteries, SCs, sensors, catalysis, etc. Recently, Kurra and co-workers [82] filtered multilayered $\text{Ti}_3\text{C}_2\text{T}_x$ electrode material on the top of delaminated $\text{Ti}_3\text{C}_2\text{T}_x$ as current collectors due to its high conductivity up to 5000 S cm^{-1} . Moreover, the d -spacing of the multilayered $\text{Ti}_3\text{C}_2\text{T}_x$ was enlarged from 9.6 to 12.9 Å because of the similar pillaring effect of Na^+ insertion in the initial cycles. In this work, authors developed a new method of fabricating the self-standing and additive-free bistacked MXene electrodes, leading to a major improvement of energy density per entire device due to the elimination of excess weight with no energy storage ability.

NASICON

NASICON with impressive features of high ion conductivity, stable structural framework and good thermal stability can be used in many fields, such as LIBs, Na-ion batteries, hybrid capacitors, solid electrolytes, gas sensors, etc. Generally, the chemical formula of NASICON materials is $\text{Na}_x\text{MM}'(\text{XO}_4)_3$ ($\text{M}/\text{M}' = \text{Ti}, \text{V}, \text{Nb}, \text{Fe}$ or Tr ; $\text{X} = \text{P}$ or S ; $x = 0, 1, 2, 3$ or 4) [83]. Among these materials, $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ ($\text{V}^{3+}/\text{V}^{4+}$ and $\text{V}^{2+}/\text{V}^{3+}$ redox conversion plateaus at 3.4 and 1.6 V) and $\text{NaTi}_2(\text{PO}_4)_3$ ($\text{Ti}^{3+}/\text{Ti}^{4+}$ conversion voltage at 2.1 V) with 3D framework structure comprising with corner-linked Ti/VO_6 octahedral and PO_4 tetrahedral have been reported for hybrid SCs [84–88]. Typically, depending on the operated platform po-

tential, $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ can be employed as both anode and cathode, but $\text{NaTi}_2(\text{PO}_4)_3$ generally acts as anode in SICs. Although the NASICON materials have many advantages, they possess poor electronic conductivity. Many researchers have made great efforts in order to solve this problem in the past few years. For example, in 2016, Thangavel *et al.* [89] reported SICs with carbon coated $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (C-NVP) as anode and AC derived from cinnamon sticks (CDCs) as cathode. HRTEM image in Fig. 5a demonstrates that the NVP is covered with a layer of carbon, which can facilitate the electrons to transfer into the C-NVP. Fig. 5b and c show that the capacitance of the SICs still retained 95% after 10,000 cycles with the maximum specific capacity of 52.58 F g^{-1} in the voltage of 0–3 V. Moreover, the Nyquist plots in the initial state and after 10,000 cycles displayed that the contact resistance between the electrode materials and electrolyte increased due to side reactions. But the charge transfer resistance decreased a little after 10,000 cycles, illustrating that the framework was stable and still practicable for reversible ions insertion (Fig. 5d). In 2017, Thangavel and co-workers [90] also reported $\text{NaTi}_2(\text{PO}_4)_3$ anchored on graphene nanosheets (GNTP) composite electrode material. TEM image in Fig. 5e demonstrates that the $\text{NaTi}_2(\text{PO}_4)_3$ particles are connected well with the graphene NSs (GNS) layers. When the SICs based on GNTP as anode and GNS as cathode were prepared and tested, Na^+ ions intercalated into the GNTP and ClO_4^- anions quickly adsorbed on the surface of GNS during the process of charging. On the contrary, Na^+ ions de-intercalated from the GNTP and ClO_4^- anions desorbed from the GNS in the discharge process (Fig. 5f). The irregular triangular GCD curves declared that there were two storage mechanisms in the SICs (Fig. 5g). Furthermore, the SICs with a low performance degradation of $\sim 0.13\%$ after 1000 cycles provided a maximum power density of 8000 W kg^{-1} , higher than other reported hybrid capacitors as shown in Fig. 5h [5,91–96]. In the work, the presence of GNS can reduce the interfacial charge transfer resistance and buffer volume changes during the sodium ion insertion into the structure, resulting in good stability of the device.

Alloys

Alloys with large theoretical capacities and high electronic conductivity superiorities have attracted much attention for many years. However, the problem of severe pulverization urgently needs to be solved. In order to optimize the properties, Yuan and co-workers [97] prepared 3D porous networks of NaBi anode by pre-sodiating the Bi

Figure 5 (a) HRTEM image of C-NVP. (b, c) GCD curves and cycling performance of the C-NVP/CDCs SICs. (d) Nyquist plots of the SICs before and after 10,000 cycles between 200 and 100 MHz. Reproduced with permission from [89]. Copyright 2016, Wiley-VCH. (e) TEM image of GNTF. The inset shows the HRTEM image of GNTF. (f) Operating mechanism of the GNTF/GNS SICs. (g) GCD curves at various current densities. (h) Comparison of the GNTF/GNS SICs performance with other systems. Reproduced with permission from [90]. Copyright 2017, Wiley-VCH.

raw material in Na-ion half cell system during the first 10 cycles in 2018. The fabricated NaBi//AC SICs showed good capacity retention of 98.6% even cycling after 1000 times as well as high energy and power densities ($106.5 \text{ W h kg}^{-1}$ and $11,100 \text{ W kg}^{-1}$) in 1.5 mol L^{-1} NaPF₆ diglyme-based electrolyte. The authors also investigated the Na⁺ storage mechanism: the NaBi anode went through the process of $\text{NaBi} \rightarrow \text{Na}_3\text{Bi}$ in the first charge process and $\text{Na}_3\text{Bi} \rightarrow \text{NaBi} \rightarrow \text{Bi}$ in the following discharge step, and then referred to the reversible reactions of $\text{Bi} \leftrightarrow \text{NaBi} \leftrightarrow \text{Na}_3\text{Bi}$. Specially, the volume expansion of the anode was significantly reduced due to the formation of porous NaBi architecture (from 256% to 65.3%), which can obviously shorten the ion diffusion distance, mitigate volume change and thus favor the re-

action kinetics.

Capacitor-type cathode materials

Carbon materials

To our best knowledge, the energy storage mechanism of the capacitor-type cathode is usually the adsorption/desorption on the surface of porous materials based on anions. Carbon materials with large specific surface area are used more often in the research of SICs, such as graphene and AC [27,30,36,43,47,53–55,59,63,65,66,70,72,76,82,84,96–100]. For example, Wang *et al.* [101] fabricated a quasi-solid-state SIC with 3D macroporous graphene as cathode and disordered carbon as anode using Na⁺ ion conducting gel polymer as electrolyte in 2015. The op-

erating potential was up to 4.2 V, much higher than those of LICs and SICs in liquid electrolytes [59,78,102]. After 1200 cycles, the capacitance still remained 85% of the initial value, demonstrating excellent cycling performance. In addition, the above mentioned SICs with GNS cathode and GNTP anode fabricated by Thangavel *et al.* [90] also exhibited good performance with the maximum power density of 8000 W kg^{-1} and a low capacitance degradation of $\sim 0.13\%$ after 1000 cycles.

Additionally, the commercial AC derived from the coal and petroleum coke has been reported as cathode in many previous literatures. Wang and co-workers [52] studied the electrochemical properties of commercial AC consisting of non-uniform nanoparticles with large surface area of $1350 \text{ m}^2 \text{ g}^{-1}$ (Fig. 6a). The commercial AC showed the operating potential of 3.0–4.3 V and stable cycling performance with the specific capacity of 43 mA h g^{-1} (Fig. 6b and c).

In view of the shortage of the fossil fuels and the in-

creasingly serious problems of the environment, biomass-derived AC possessing high surface area, high electrical conductivity, low cost, abundant resources, adjustable pore structure and chemical stability have been studied in recent years, such as peanut shells, rice and fish scales [28,29,31,39,43,44,46,48,50,55,60,62,89,103–108]. In 2015, Ding *et al.* [102] prepared both carbon electrode materials from a single precursor of biomass waste peanut shells for the first time (Fig. 6d). During the preparation, the peanut shell was firstly divided into the inner and outer parts through roughly grinding. The outer part was transformed into peanut shell NS carbon (PSNC) containing 35.4% mesopores ($2396 \text{ m}^2 \text{ g}^{-1}$) as cathode through hydrothermal and subsequently KOH activation processes (Fig. 6e). The inner part was directly carbonized at 1200°C in argon and then activated at 300°C in air to obtain peanut shell ordered carbon (PSOC) as anode, along with the interlayer spacing (d_{002}) of $3.79 \text{ \AA}$. The fabricated SICs delivered high energy and power densities

Figure 6 (a–c) Morphological and electrochemical performance of the AC cathode. Reproduced with permission from [52]. Copyright 2018, Wiley-VCH. (d) The process of cathode/anode materials synthesis and charge storage mechanisms of the SICs. (e) SEM image of PSNC-3-800. (f) Ragone plot of the PSNC-3-800/PSOC-A at different temperatures. Reproduced with permission from [102]. Copyright 2015, Royal Society of Chemistry. (g) Schematic diagram of the SICs with j-HPC. (h) SEM image of j-HPC. (i) GCD curves of the pre-sodiated j-HPC/j-HPC SICs at different current densities. Reproduced with permission from [109]. Copyright 2018, Elsevier.

of 201 W h kg⁻¹ and 16,500 W kg⁻¹ (Fig. 6f), respectively. Encouragingly, when tested at 65°C, this device exhibited higher power density of 34,000 W kg⁻¹ at the energy density of 60 W h kg⁻¹. In this work, the researchers investigated that the capacitance of the PSNC came from not only the anions adsorption, but also the pseudocapacitance of the defects and oxygen functionalities. In 2018, Phattharasupakun *et al.* [109] successfully prepared Jasmine rice-derived hierarchical porous carbon (j-HPC) through a solvothermal method followed by activation processes for the first time (Fig. 6g and h). The as-prepared porous carbon had large specific surface area and average pore diameter of 2377 m² g⁻¹ and 2.53 nm, facilitating the anions adsorption on the surface of the materials and Na-ion intercalation. When assembled to SICs based on j-HPC electrodes, the device with the working voltage of 1.0–3.8 V displayed the maximum energy and power densities of 116.7 W h kg⁻¹ and 11,121.54 W kg⁻¹, respectively, higher than those of previously reported EDHPC//EDHPC and NOFC//PSNC systems (Fig. 6i) [44,108].

These carbon electrodes derived from various biomass materials with low cost, rich reserves, environment-friendliness and cyclic utilization have the features of porous architecture, large surface area, good electrical conductivity and heteroatom introduction, leading to

potential application in sodium-ion storage [27,29–31,39,40,42–44,101–104,108–112]. As a consequence, we summarized the carbonaceous materials for positive and negative electrodes in SICs in Table 1.

MXenes

2D MXenes have metallic conductivity and relatively large specific surface area as well as hydrophilia so that they can be used as cathode materials in the SICs. For example, in 2015, Dall'Agnese *et al.* [36] prepared the V₂C layered electrode materials from simple etching process and investigated the sodiation mechanism in half cell for the first time. Subsequently, they fabricated a SIC based on V₂C as cathode and hard carbon (HC) as anode in 1 mol L⁻¹ NaPF₆ organic electrolyte (Fig. 7a). This SICs with a maximum voltage of 3.5 V showed prospective applications in ESS (Fig. 7b and c).

In 2017, Zhang *et al.* [47] prepared Ti₃C₂T_x NSs with expanded interlayer distance through HF etching and ultrasonic treatment at room temperature, as shown in Fig. 7d and e. For the first time, using Ti₃C₂T_x as cathode and MnO₂ as anode in Na₂SO₄ aqueous electrolyte, the researchers assembled the SICs with outstanding rate performance. Even when the current density increased to 250 times of the initial value, the capacity retention still retained 38% (Fig. 7f). The obtained SIC with a safe

Table 1 Summary of SICs based on both carbonaceous anode and cathode

Anode/cathode	Electrolyte	Voltage (V)	Max E (W h kg ⁻¹)/max P (W kg ⁻¹)	Cycle performance	Ref.
j-HPC// j-HPC	1 mol L ⁻¹ NaPF ₆	1–3.8	116.70/11,121.54	90% over 5000 cycles	[109]
CS-800//CS-800-6	1 mol L ⁻¹ NaClO ₄	2–4	52.2/3000	85.7 over 2000 cycles	[39]
HPC-550//HPC-800	1 mol L ⁻¹ NaClO ₄	0–4	103.2/15,900	81.1% over 2500 cycles	[31]
3DCFs//SDAC	1 mol L ⁻¹ NaClO ₄	0–4	133.2/20,000	86% over 4000 cycles	[104]
DCDC-K//MCC	1 mol L ⁻¹ NaClO ₄	0–4	110.8/12,100	85% over 10000 cycles	[29]
AC//P-aCNs	1 mol L ⁻¹ NaClO ₄	0–2	27.9/1379.31	96% over 100,000 cycles	[30]
HC//BG	1 mol L ⁻¹ NaPF ₆	0–4	108/6100	97% over 5000 cycles	[110]
EDHPC//EDHPC	1 mol L ⁻¹ NaClO ₄	0–4	84/9053	67% over 5000 cycles	[44]
NOFC//PSNC	1 mol L ⁻¹ NaClO ₄	0–4	111/14,550	90% over 5000 cycles	[108]
DC//NC	1 mol L ⁻¹ NaPF ₆	0–4.4	157/2356	70% over 1000 cycles	[111]
GDY-NS//AC	1 mol L ⁻¹ NaPF ₆	2–4	182.3/15,000	90% over 3000 cycles	[42]
HP-CNWs//FM	1 mol L ⁻¹ NaPF ₆	0.5–4.2	130.6/15,260	85.4% over 3000 cycles	[103]
3DFC//3DFAC	1 mol L ⁻¹ NaClO ₄	0–4	111/20,000	75.6% over 15,000 cycles	[112]
MCMC/AC	1 mol L ⁻¹ NaPF ₆	1–4	93.5/2832	98.3% over 3000 cycles	[40]
DC//MG	1 mol L ⁻¹ NaClO ₄	0–4.2	168/2432	85% over 1200 cycles	[101]
PSOC//PNSC	1 mol L ⁻¹ NaClO ₄	1.5–4.2	201.76/16,500	72% over 10,000 cycles	[102]
SCN-A//SCN-A	1 mol L ⁻¹ NaClO ₄	0–4	112/12,000	85% over 3000 cycles	[43]
UTH-CN//AC	1 mol L ⁻¹ NaClO ₄	0.5–4	110/10,000	70% over 1000 cycles	[27]

Figure 7 (a) Schematic diagram of the HC//V₂C SICs. (b) GCD curves at different rates. (c) Capacity *versus* cycle number. Reproduced with permission from [36]. Copyright 2015, American Chemical Society. (d, e) SEM images of Ti₃C₂T_x before and after ultrasonic treatment. (f, g) Rate performance and cycling properties of the MnO₂/Ti₃C₂T_x SICs. Reproduced with permission from [47]. Copyright 2017, Wiley-VCH.

voltage of 0–2.4 V showed superior cycling stability that 95.9% of the capacitance retention and over 90% of the Coulombic efficiency still retained after 450 cycles (Fig. 7g). This aqueous hybrid SICs based on Ti₃C₂T_x with expanded interlayer distance and efficient ion transport path are low-cost, safe and easily mass-produced in the future.

Prussian blue

PB and its analogues (PBA) with the advantages of 3D open framework, structure stability, large lattice void, high theoretical capacity (e.g., 170 mA h g⁻¹ of Na₂FeFe(CN)₆) and the low-cost synthesis are good electrode materials for energy storage [113–115]. The general chemical formula of PB/PBA is A_xP_y[R(CN)₆]_z·nH₂O, (A = K⁺ or Na⁺, P/R = Fe²⁺, Fe³⁺, Co²⁺, Mn²⁺, Ni²⁺, Zn²⁺, Cu²⁺, etc.) The P and R cations connected with –C≡N construct the cubic framework, which includes interstitial A sites [116]. PB with cubic crystal structure contains Fe²⁺ and Fe³⁺ ions on the face-centered cubic lattice in turn

(Fig. 8a). When the framework structure of PB allows multiple species to occupy the A, P and R sites, the PBA can be obtained. Recently, PB and PBA as cathode materials in energy storage devices have been widely reported [49,117–119]. For instance, Lu *et al.* [49] designed the manganous hexacyanoferrate (MnHCF) material with a specific surface area of 218 m² g⁻¹ by a co-precipitation method. When the SICs were prepared based on MnHCF as cathode and Fe₃O₄/rGO as anode in Na₂SO₄ aqueous electrolyte, the devices with the operating potential of 0–1.8 V exhibited high energy and power densities of 43.2 W h kg⁻¹ and 2183.5 W kg⁻¹ as well as 82.2% of the capacitance retention and 99.5% of the Coulombic efficiency after 1000 cycles (Fig. 8b and c).

Additionally, in 2015, Lu *et al.* [117] also obtained Co-based PBA framework using Co(NO₃)₂ and K₃Fe(CN)₆ solution by a co-precipitation method. These as-prepared CoHCF with porous network consisted of polydisperse nanoparticles as shown in Fig. 8d. After fabricating SICs by using CoHCF as cathode and carbon micro-spheres

Figure 8 (a) Schematic illustration of the crystal structure of MnHCF. (b) The cycling performance of MnHCF//Fe₃O₄/rGO SICs. (c) Ragone plots of the hybrid device. The inset shows that a LED was lighted by two SICs in series. Reproduced with permission from [49]. Copyright 2015, Royal Society of Chemistry. (d) TEM image of CoHCF nanoparticles. The inset is the HRTEM image of CoHCF. (e, f) GCD curves and Ragone plots of the CoHCF//CMS SICs. Reproduced with permission from [117]. Copyright 2015, Elsevier. (g, h) Morphology of the CoHCF submicrocube. (i, j) GCD curves and Ragone plots of the CoHCF//AC hybrid SICs. Reproduced with permission from [119]. Copyright 2017, Elsevier.

(CMS) as anode, a high voltage of 2 V was obtained in Na₂SO₄ aqueous electrolyte (Fig. 8e). Furthermore, the fabricated SICs delivered a high energy density (54.4 W h kg⁻¹ at 800 W kg⁻¹) and power density (5037 W kg⁻¹ at 37.8 W h kg⁻¹) as shown in Fig. 8f. Except for as cathode material, MnHCF can also be used as sacrificial template to produce other hollow structured PBA electrodes due to its high solubility constant ($K=1.9\times 10^{-3}$). In 2017, Wang and co-workers [119] synthesized hollow submicrocube CoHCF with extreme challenge in Co(NO₃)₂ and MnHCF suspension through the cations exchange method (Fig. 8g and h). These prepared hollow submicrocubes with increased surface area (693 m² g⁻¹) and more available active sites can relieve structural strain during the electrochemical reactions. The fabricated aqueous SICs of CoHCF//AC showed improved working potential window of 0–2 V and power density of 21,100 W kg⁻¹ (Fig. 8i and j). Given

the features of easy preparation, low costs and capability to be used in aqueous electrolytes, the PB and PBA frameworks with vacant spaces and open channels can significantly facilitate the alkali ions transport and have great promise in future ESS.

Other Na-ion based cathode materials

Sodium metal phosphates (NaMPO₄, M represents Ni, Mn, Co and Fe) are prospectively used as cathodes with the characteristics of thermal stability attributing to the maricite structure and high working voltage owing to the inductive effect. For instance, in 2014, Senthilkumar *et al.* [120] synthesized NaMPO₄ (M= Mn, Co, Ni) by solution combustion processes, respectively. These three as-prepared compounds exhibited different specific capacitances of 368 F g⁻¹ (NaNiPO₄), 249 F g⁻¹ (NaCoPO₄) and 163 F g⁻¹ (NaMnPO₄) at the current density of 2 mA cm⁻² in a three-electrode system of 1 mol L⁻¹ NaOH solution.

Furthermore, the AC//NaNiPO₄ SIC device delivered the high energy and power densities of 20 W h kg⁻¹ and 1358 W kg⁻¹ calculated from GCD curves. According to the conductivity sequence of U_{Fe} (3.71 eV) < U_{Mn} (3.92 eV) < U_{Co} (5.05 eV) < U_{Ni} (5.26 eV) in the standard Hubbard model (DFT+U method), the mixed sodium transition metal phosphate NaMn_{1/3}Co_{1/3}Ni_{1/3}PO₄ has attracted much attention because of its narrowed band gap and enhanced conductivity. In 2015, Sundaram and co-workers [121] prepared the NaMn_{1/3}Co_{1/3}Ni_{1/3}PO₄ maricite structure *via* a sol-gel process. With NaMn_{1/3}Co_{1/3}Ni_{1/3}PO₄ as cathode and carbon as anode, the fabricated SIC device achieved an energy density of 50 W h kg⁻¹ at the power density of 180 W kg⁻¹ in 1 mol L⁻¹ NaPF₆ non-aqueous electrolyte.

Na₃V₂(PO₄)₃ (NVP) can be used as both anode and cathode electrodes for SIC, in which one Na ion can easily insert into or two Na ions extract from the NVP host with two distinctive plateaus of 1.6 and 3.4 V, respectively. For example, using porous C/V₂O₅ composite as precursor, Jian *et al.* [86] prepared NVP electrode material with improved electrical conductivity through an ambient hydrolysis deposition method. The fabricated symmetric Na-ion pseudocapacitor in NaPF₆ organic electrolyte exhibited the features of high reversibility, high-rate as well as low cost and bridged the performance gap between the batteries and SCs.

In summary, Na-ion based transition metal compounds with 3D porous framework, large-sized tunnels, improved conductivity and cost-effective characteristics can be used as electrodes in sodium ion storage systems. As mentioned above, the chosen Na_{0.44}MnO₂ and Na_{0.21}MnO₂ with excellent cycling stability and good rate performance have been reported as cathodes in the Ti₃C₂T_x/CNT//Na_{0.44}MnO₂ and rGO//Na_{0.21}MnO₂ SICs, respectively [41,80]. Moreover, the alluaudite-type Na₂Fe₂(SO₄)₃ with a theoretical capacity of 120 mA h g⁻¹ and a high redox voltage of 3.8 V has been used as cathode to fabricate hybrid sodium ion pseudocapacitor by Zhu *et al.* [77]. According to this work, it is suggested that other alluaudite-type compounds of Na_{2-x}M₂(SO₄)₃ (M = Ti, Co, Mn, Mg, V, Ni or VO) are also worthy of being explored as electrode materials for sodium ion storage in the future.

ELECTROLYTES

The electrolytes used in the SIC devices commonly consist of organic electrolytes, aqueous electrolytes and ionic liquid electrolytes. Among these electrolytes, the ionic conductivities of aqueous electrolytes are the highest (up

to 1 S cm⁻¹). The aqueous electrolytes own the low cost and safe features. However, the electrochemical stable window was limited to 1.23 V due to the decomposition of water [122]. Compared with aqueous systems, organic electrolytes possess wider potential window (~4 V) because of their higher decomposition voltage, whereas they are not safe with the disadvantages of toxicity, volatility and low flash point (~80°C) for energy storage devices [122]. Additionally, ionic liquid electrolytes with non-flammability, low-volatility and high ignition temperature (>300°C) other than low conductivity and high viscosity can provide large potential windows and stable solid electrolyte interphase (SEI) film with the absence of dendrites when applied in electrochemical storage systems [123].

Generally, the aqueous systems including acid-based, alkali-based and neutral electrolytes are often involved in recent years [47,68,84,117,124–126]. For example, the reported Na₄Mn₉O₁₈//AC hybrid capacitor system [127] in 1 mol L⁻¹ NaCl aqueous solution displayed stable cycling performance (Fig. 9a and b). In 2 mol L⁻¹ Na₂SO₄ aqueous electrolyte, the fabricated Na_{0.21}MnO₂//rGO SICs [41] displayed an operating voltage of 2.7 V, much higher than other aqueous SICs (Fig. 9c) [47,68,84,127]. It is concluded that the strong bonding of Mn³⁺ with adsorbed OH⁻ ions in these SICs can lead to higher overpotential of Mn-based compounds towards water oxidation. In addition, the authors compared the electrochemical performances of the NaMPO₄ (M = Mn, Co, Ni) in various Na-based aqueous electrolytes (Fig. 9d). The specific capacitances of NaMPO₄ in 1 mol L⁻¹ NaOH aqueous solution were much higher than that in Na₂SO₄, NaCl and NaNO₃ solutions, which was derived from the smaller ionic solvation radius of OH⁻ (3.00 Å) than those of NO₃⁻ (3.35 Å), Cl⁻ (3.32 Å) and SO₄²⁻ (3.79 Å). Furthermore, the pseudocapacitance reactions in alkali condition also contributed to improve the electrochemical performance [120]. Significantly, the “water-in-salt” electrolyte with high salt concentration has been investigated in recent years. Compared with the common aqueous solution, the high-concentration electrolyte can provide wider as well as more stable voltage window and more easily form the passivation layer on the surface of electrode materials, leading to high electrochemical performance. For instance, in 17 mol L⁻¹ NaClO₄ aqueous electrolyte with the maximum window of 2.75 V, Zhang *et al.* [124] successfully assembled the PI//porous carbon microspheres SICs. The enhanced operating voltage of 2 V guaranteed that the SICs delivered a high energy density (65 W h kg⁻¹) and a high power density (20,000 W kg⁻¹).

Figure 9 (a) Schematic of desalination by hybrid capacitive deionization (HCDI). (b) Specific capacity versus cycle number. Reproduced with permission from [127]. Copyright 2014, Royal Society of Chemistry. (c) GCD profiles of the Na₄Mn₉O₁₈//AC device in 2 mol L⁻¹ Na₂SO₄ aqueous electrolyte. Reproduced with permission from [41]. Copyright 2017, Wiley-VCH. (d) Capacitance of NaMPO₄ (M = Ni, Co, Fe and Mn) in different aqueous electrolytes. Reproduced with permission from [120]. Copyright 2014, Royal Society of Chemistry. (e) CV curves of the two half cells and hybrid Na₂Ti₂O₄(OH)₂/RHDPC-KOH SIC in 1 mol L⁻¹ NaPF₆ organic electrolyte. Reproduced with permission from [106]. Copyright 2017, Elsevier. (f) Schematic illustration of the charge-storage mechanisms for the MoSe₂/G//AC in 1 mol L⁻¹ NaClO₄ organic electrolyte. Reproduced with permission from [72]. Copyright 2018, Elsevier. (g) Voltage profiles of the SICs at 25 mA g⁻¹. (h) Ragone plot of the Li₄Ti₅O₁₂//AC SICs with a comparison to the reports. Reproduced with permission from [100]. Copyright 2018, Elsevier.

Presently, the organic electrolytes composed of NaClO₄ or NaPF₆ in cyclic carbonate esters (PC and EC) and linear carbonates (EMC, DMC and DEC) with a certain ratio have been widely used in SICs [28–30,42,48,52,101,108,110,112]. Additionally, 5% fluoroethylene carbonate (FEC) as additive was frequently added into the above organic systems, which can contribute to improving passivation and suppressing the side reactions (Fig. 9e and f) [72,106]. In these systems, Na⁺ cations were stored through insertion process and ClO₄⁻/PF₆⁻ anions were adsorbed on the surface of the cathode, simultaneously.

The ionic liquid electrolytes with various advantages

are highlighted in the research of SICs in spite of their high viscosity and low conductivity [100,128,129]. When used at high temperature below the melting point of sodium (98°C), their disadvantages can be effectively alleviated. Fig. 9g shows the GCD curves of the SICs [100] based on Li₄Ti₅O₁₂ as anode and AC as cathode with 0.8 mol L⁻¹ sodium bis(fluorosulfonyl)imide (Na-TFSI) in 1-methyl-1-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide (PMPyrr-TFSI) electrolyte. The SIC devices operated from 1.0 to 4.0 V at the current density of 25 mA g⁻¹ and achieved 69% capacitance retention after 1500 cycles. However, the cycling stability is barely sa-

tisfactory because of the large ionic radius of Na^+ . The calculated specific energy and power densities were 90 W h kg^{-1} and 1780 W kg^{-1} , superior than other organic electrolyte systems of AC// $\text{Na}_2\text{Ti}_3\text{O}_7$ (1.5 mol L^{-1} NaClO_4 PC/DMC) and AC// TiO_2 (1 mol L^{-1} NaClO_4 EC/PC) (Fig. 9h) [54,59].

PRESENTATION OF SICs AND THEIR POTENTIAL APPLICATIONS

Generally, there are three types of SICs: coin, pouch and flexible packaging. The liquid and quasi-solid-state electrolytes both can be used in the flexible packaging cells. Specially, the common quasi-solid-state electrolyte in SICs was based on poly(vinylidene fluoride-hexafluoropropylene) (P(VDF-HFP)) [60,62,101]. Briefly, the P(VDF-HFP) was firstly dissolved in the mixture of dimethyl formamide (DMF) and distilled water with a certain ratio. The solution was cast onto a clean glass plate and then immersed into hot water to obtain a homogeneous white membrane. After being dried in the vacuum, the white membrane was finally soaked in the organic electrolyte to get the quasi-solid-state electrolyte.

Additionally, other cellulose-based quasi-solid-state electrolytes can be also used in SICs [130–132]. In the preparation, hydroxyethyl cellulose (HEC), polyethylene oxide (PEO) and sodium perchlorate (NaClO_4) were first dissolved in deionized water, followed by adding silicon dioxide (SiO_2). Then the solution was transferred into a Teflon petri dish and dried to form a cellulose-based membrane (HEC-PEO).

After the successful fabrication of SICs based on various electrode materials and electrolytes with high electrochemical performance, the practical use should be considered. However, the application field of the SICs was less reported except for powering the LED lamps and fans [40,52,58,62]. As shown in Fig. 10a and b, the LED bulb and fan were powered by a GDY-NS//AC coin SIC and a graphitic mesocarbon microbead (MCMCB)//AC SIC with hard aluminum shell, respectively [40,42]. Fig. 10c presents a table lamp lighted by a flexible all-solid-state $\text{Na}_2\text{Ti}_3\text{O}_7$ //PSC SIC [62]. Additionally, the SICs with high energy and power densities can be hopefully applied in EVs and urban rail transports. As an example, regenerative braking energy of urban rail transport can be

Figure 10 (a–c) The LED bulb, fan and table lamp were powered by coin, pouch and flexible all-solid-state SICs (from left to right). Reproduced with permission from [42], [40] and [62]. Copyright 2017, American Chemical Society; Copyright 2015, Elsevier and Copyright 2016, American Chemical Society, respectively. (d, e) Schematic diagram of ESSs operation in urban rail on-board and way-side. Reproduced with permission from [133]. Copyright 2013, Elsevier.

efficiently stored in the ESS, which can be designed on-board or way-side [133]. During the braking process, the energy was collected and stored in the on-board ESS, which can be employed to charge the vehicle itself when it was accelerating as shown in Fig. 10d. Similarly, the regenerative braking energy obtained from one vehicle can be conveyed to the way-side ESS momentarily, and then used on any vehicle that needs to accelerate as shown in Fig. 10e. This application can decrease the power peak value demanded in the acceleration and save energy cost, significantly.

CONCLUSIONS AND OUTLOOK

In this review, the latest development of SICs has been systematically summarized. We first classify the frequent electrode materials for the anode and cathode and then sum up the approaches to improve the electrochemical performance from the aspects of lattice distance, heteroatom doping, specific surface area and electronic conductivity. Notably, heteroatom modification can enhance the wettability of the voids, which is beneficial to the contact between the electrolyte and the electrode and delivering pseudocapacitive behaviors. At the same time, some micro/nanostructured materials can reduce the distance of Na-ion transport, effectively improving the reaction kinetics. Moreover, incorporating carbon materials into the electrodes contributes to boosting the electronic conductivity. Meanwhile, the respective working conditions of the electrolytes as well as the presentation and potential application of the SICs in urban rail transport are also introduced in detail.

Although some progress has been made in SICs, there are still some shortcomings to be solved. For example, one major challenge is how to overcome the sluggish diffusion behavior of Na-ion to balance the kinetics with cathode adsorption/desorption. Consequently, further research emphasis should be paid attention to as follows:

(i) Although there are many anode materials used in SICs, the electrochemical performance is far behind the demands of practical application. Developing new hosts with large lattice space available for Na^+ ions insertion as well as 3D nanostructured arrays germinated on the current collectors without binders or additives are extremely urgent.

(ii) Besides, the SICs designed with both carbon-based anode and cathode prospectively supply good electrochemical properties due to good electronic conductivity, mesoporous structures and high specific surface area. Moreover, developing the biomass-derived carbon electrodes can not only decrease the material costs but also

promote waste recycling.

(iii) The high energy density is mainly derived from high voltage, which is dependent on the working potential of the electrolyte. It is worth noting that ionic liquid electrolytes possess high voltage and relatively safe features. Different conjugation of anions and cations may improve the ionic conductivity and potential window of the ionic liquid electrolytes. Meanwhile, the SICs can be well used in a wide range of temperature. Additionally, the “water-in-salt” electrolytes that can get rid of the limitation of water electrolysis should be optimized to achieve higher voltage.

(iv) The flexible SICs will be a promising filed in the future, which can be used in our daily life. However, the corresponding reports are few according to the current situation. As a consequence, more attention should be paid to the all-solid-state gel sodium-containing electrolyte and flexible substrates.

(v) At the moment, the application of the SICs are primarily concentrated on lighting LED lamps. Whereas, the integration of the SICs with other sensors, detectors and energy harvester is important for achieving more practical values. In this respect, taking more effort on the integration can efficiently stimulate the development of the SICs.

(vi) Despite the rapid development of materials science, the theory calculations should be enhanced in the field of SICs, which can contribute to establishing models and providing more convincing evidence for the experimental results, simultaneously.

Received 4 September 2019; accepted 19 September 2019;
published online 4 November 2019

- 1 Lu X, Yu M, Wang G, *et al.* Flexible solid-state supercapacitors: design, fabrication and applications. *Energy Environ Sci*, 2014, 7: 2160–2181
- 2 Lim E, Kim H, Jo C, *et al.* Advanced hybrid supercapacitor based on a mesoporous niobium pentoxide/carbon as high-performance anode. *ACS Nano*, 2014, 8: 8968–8978
- 3 Simon P, Gogotsi Y, Dunn B. Where do batteries end and supercapacitors begin? *Science*, 2014, 343: 1210–1211
- 4 Zuo W, Li R, Zhou C, *et al.* Battery-supercapacitor hybrid devices: recent progress and future prospects. *Adv Sci*, 2017, 4: 1600539
- 5 Kim H, Cho MY, Kim MH, *et al.* A novel high-energy hybrid supercapacitor with an anatase TiO_2 -reduced graphene oxide anode and an activated carbon cathode. *Adv Energy Mater*, 2013, 3: 1500–1506
- 6 Won JH, Jeong HM, Kang JK. Synthesis of nitrogen-rich nanotubes with internal compartments having open mesoporous channels and utilization to hybrid full-cell capacitors enabling high energy and power densities over robust cycle life. *Adv En-*

- ergy Mater, 2017, 7: 1601355
- 7 Zhang F, Zhang T, Yang X, *et al.* A high-performance supercapacitor-battery hybrid energy storage device based on graphene-enhanced electrode materials with ultrahigh energy density. *Energy Environ Sci*, 2013, 6: 1623–1632
 - 8 Wang F, Liu Z, Wang X, *et al.* A conductive polymer coated MoO₃ anode enables an Al-ion capacitor with high performance. *J Mater Chem A*, 2016, 4: 5115–5123
 - 9 Larcher D, Tarascon JM. Towards greener and more sustainable batteries for electrical energy storage. *Nat Chem*, 2015, 7: 19–29
 - 10 Yun YS, Cho SY, Shim J, *et al.* Microporous carbon nanoplates from regenerated silk proteins for supercapacitors. *Adv Mater*, 2013, 25: 1993–1998
 - 11 Lee SW, Gallant BM, Byon HR, *et al.* Nanostructured carbon-based electrodes: bridging the gap between thin-film lithium-ion batteries and electrochemical capacitors. *Energy Environ Sci*, 2011, 4: 1972
 - 12 Ma Y, Chang H, Zhang M, *et al.* Graphene-based materials for lithium-ion hybrid supercapacitors. *Adv Mater*, 2015, 27: 5296–5308
 - 13 Li B, Dai F, Xiao Q, *et al.* Activated carbon from biomass transfer for high-energy density lithium-ion supercapacitors. *Adv Energy Mater*, 2016, 6: 1600802
 - 14 Yang M, Zhong Y, Ren J, *et al.* Fabrication of high-power Li-ion hybrid supercapacitors by enhancing the exterior surface charge storage. *Adv Energy Mater*, 2015, 5: 1500550
 - 15 Aravindan V, Gnanaraj J, Lee YS, *et al.* Insertion-type electrodes for nonaqueous Li-ion capacitors. *Chem Rev*, 2014, 114: 11619–11635
 - 16 Gu H, Zhu YE, Yang J, *et al.* Nanomaterials and technologies for lithium-ion hybrid supercapacitors. *ChemNanoMat*, 2016, 2: 578–587
 - 17 Yu X, Zhan C, Lv R, *et al.* Ultrahigh-rate and high-density lithium-ion capacitors through hybridizing nitrogen-enriched hierarchical porous carbon cathode with prelithiated microcrystalline graphite anode. *Nano Energy*, 2015, 15: 43–53
 - 18 Puthusseri D, Aravindan V, Anothumakkool B, *et al.* From waste paper basket to solid state and Li-HEC ultracapacitor electrodes: A value added journey for shredded office paper. *Small*, 2014, 10: 4395–4402
 - 19 Wang F, Wang C, Zhao Y, *et al.* A quasi-solid-state Li-ion capacitor based on porous TiO₂ hollow microspheres wrapped with graphene nanosheets. *Small*, 2016, 12: 6207–6213
 - 20 Slater MD, Kim D, Lee E, *et al.* Sodium-ion batteries. *Adv Funct Mater*, 2013, 23: 947–958
 - 21 Ding J, Hu W, Paek E, *et al.* Review of hybrid ion capacitors: from aqueous to lithium to sodium. *Chem Rev*, 2018, 118: 6457–6498
 - 22 Wang H, Zhu C, Chao D, *et al.* Nonaqueous hybrid lithium-ion and sodium-ion capacitors. *Adv Mater*, 2017, 29: 1702093
 - 23 Aravindan V, Ulaganathan M, Madhavi S. Research progress in Na-ion capacitors. *J Mater Chem A*, 2016, 4: 7538–7548
 - 24 Li F, Zhou Z. Micro/nanostructured materials for sodium ion batteries and capacitors. *Small*, 2018, 14: 1702961
 - 25 Zhu C, Yang P, Chao D, *et al.* Heterogeneous nanostructures for sodium ion batteries and supercapacitors. *ChemNanoMat*, 2015, 1: 458–476
 - 26 Luo J, Fang C, Jin C, *et al.* Tunable pseudocapacitance storage of MXene by cation pillaring for high performance sodium-ion capacitors. *J Mater Chem A*, 2018, 6: 7794–7806
 - 27 Yun YS, Cho SY, Kim H, *et al.* Ultra-thin hollow carbon nanospheres for pseudocapacitive sodium-ion storage. *ChemElectroChem*, 2015, 2: 359–365
 - 28 Kim NR, Yun YS, Song MY, *et al.* Citrus-peel-derived, nanoporous carbon nanosheets containing redox-active heteroatoms for sodium-ion storage. *ACS Appl Mater Interfaces*, 2016, 8: 3175–3181
 - 29 Dong G, Wang H, Liu W, *et al.* Nitrate salt assisted fabrication of highly N-doped carbons for high-performance sodium ion capacitors. *ACS Appl Energy Mater*, 2018, acaem.8b01166
 - 30 Park SK, Kwon SH, Lee SG, *et al.* 10⁵ Cyclable pseudocapacitive Na-ion storage of hierarchically structured phosphorus-incorporating nanoporous carbons in organic electrolytes. *ACS Energy Lett*, 2018, 3: 724–732
 - 31 Liu M, Niu J, Zhang Z, *et al.* Porous carbons with tailored heteroatom doping and well-defined porosity as high-performance electrodes for robust Na-ion capacitors. *J Power Sources*, 2019, 414: 68–75
 - 32 Zou K, Cai P, Liu C, *et al.* A kinetically well-matched full-carbon sodium-ion capacitor. *J Mater Chem A*, 2019, 7: 13540–13549
 - 33 Zou G, Hou H, Foster CW, *et al.* Advanced hierarchical vesicular carbon Co-doped with S, P, N for high-rate sodium storage. *Adv Sci*, 2018, 5: 1800241
 - 34 Hou H, Banks CE, Jing M, *et al.* Carbon quantum dots and their derivative 3D porous carbon frameworks for sodium-ion batteries with ultralong cycle life. *Adv Mater*, 2015, 27: 7861–7866
 - 35 Kuratani K, Yao M, Senoh H, *et al.* Na-ion capacitor using sodium pre-doped hard carbon and activated carbon. *Electrochim Acta*, 2012, 76: 320–325
 - 36 Dall'Agnese Y, Taberna PL, Gogotsi Y, *et al.* Two-dimensional vanadium carbide (MXene) as positive electrode for sodium-ion capacitors. *J Phys Chem Lett*, 2015, 6: 2305–2309
 - 37 Li Z, Bommier C, Chong ZS, *et al.* Mechanism of Na-ion storage in hard carbon anodes revealed by heteroatom doping. *Adv Energy Mater*, 2017, 7: 1602894
 - 38 Qiu S, Xiao L, Sushko ML, *et al.* Manipulating adsorption-insertion mechanisms in nanostructured carbon materials for high-efficiency sodium ion storage. *Adv Energy Mater*, 2017, 7: 1700403
 - 39 Wang S, Wang R, Zhang Y, *et al.* Scalable and sustainable synthesis of carbon microspheres via a purification-free strategy for sodium-ion capacitors. *J Power Sources*, 2018, 379: 33–40
 - 40 Han P, Han X, Yao J, *et al.* High energy density sodium-ion capacitors through co-intercalation mechanism in diglyme-based electrolyte system. *J Power Sources*, 2015, 297: 457–463
 - 41 Karikalan N, Karuppiiah C, Chen SM, *et al.* Three-dimensional fibrous network of Na_{0.21}MnO₂ for aqueous sodium-ion hybrid supercapacitors. *Chem Eur J*, 2017, 23: 2379–2386
 - 42 Wang K, Wang N, He J, *et al.* Preparation of 3D architecture graphdiyne nanosheets for high-performance sodium-ion batteries and capacitors. *ACS Appl Mater Interfaces*, 2017, 9: 40604–40613
 - 43 Wang H, Mitlin D, Ding J, *et al.* Excellent energy–power characteristics from a hybrid sodium ion capacitor based on identical carbon nanosheets in both electrodes. *J Mater Chem A*, 2016, 4: 5149–5158
 - 44 Liu X, Wang H, Cui Y, *et al.* High-energy sodium-ion capacitor assembled by hierarchical porous carbon electrodes derived from enteromorpha. *J Mater Sci*, 2018, 53: 6763–6773
 - 45 Chen Z, Augustyn V, Jia X, *et al.* High-performance sodium-ion pseudocapacitors based on hierarchically porous nanowire com-

- posites. *ACS Nano*, 2012, 6: 4319–4327
- 46 Kiruthiga R, Nithya C, Karvembu R, *et al.* Reduced graphene oxide embedded V_2O_5 nanorods and porous honey carbon as high performance electrodes for hybrid sodium-ion supercapacitors. *Electrochim Acta*, 2017, 256: 221–231
 - 47 Zhu K, Zhang H, Ye K, *et al.* Two-dimensional titanium carbide MXene as a capacitor-type electrode for rechargeable aqueous Li-ion and Na-ion capacitor batteries. *ChemElectroChem*, 2017, 4: 3018–3025
 - 48 Ramakrishnan K, Nithya C, Karvembu R. High-performance sodium ion capacitor based on MoO_2 @rGO nanocomposite and goat hair derived carbon electrodes. *ACS Appl Energy Mater*, 2018, 1: 841–850
 - 49 Lu K, Li D, Gao X, *et al.* An advanced aqueous sodium-ion supercapacitor with a manganous hexacyanoferrate cathode and a Fe_3O_4 /rGO anode. *J Mater Chem A*, 2015, 3: 16013–16019
 - 50 Li H, Zhu Y, Dong S, *et al.* Self-assembled Nb_2O_5 nanosheets for high energy–high power sodium ion capacitors. *Chem Mater*, 2016, 28: 5753–5760
 - 51 Lim E, Jo C, Kim MS, *et al.* High-performance sodium-ion hybrid supercapacitor based on Nb_2O_5 @carbon core-shell nanoparticles and reduced graphene oxide nanocomposites. *Adv Funct Mater*, 2016, 26: 3711–3719
 - 52 Wang X, Li Q, Zhang L, *et al.* Caging Nb_2O_5 nanowires in PECVD-derived graphene capsules toward bendable sodium-ion hybrid supercapacitors. *Adv Mater*, 2018, 30: 1800963
 - 53 Wu Y, Fan X, Gaddam RR, *et al.* Mesoporous niobium pentoxide/carbon composite electrodes for sodium-ion capacitors. *J Power Sources*, 2018, 408: 82–90
 - 54 Le Z, Liu F, Nie P, *et al.* Pseudocapacitive sodium storage in mesoporous single-crystal-like TiO_2 -graphene nanocomposite enables high-performance sodium-ion capacitors. *ACS Nano*, 2017, 11: 2952–2960
 - 55 Zhu YE, Yang L, Sheng J, *et al.* Fast sodium storage in TiO_2 @CNT@C nanorods for high-performance Na-ion capacitors. *Adv Energy Mater*, 2017, 7: 1701222
 - 56 Babu B, Ullattil SG, Prasannachandran R, *et al.* Ti^{3+} induced brown TiO_2 nanotubes for high performance sodium-ion hybrid capacitors. *ACS Sustain Chem Eng*, 2018, 6: 5401–5412
 - 57 Gao L, Chen S, Zhang L, *et al.* High performance sodium ion hybrid supercapacitors based on $Na_2Ti_3O_7$ nanosheet arrays. *J Alloys Compd*, 2018, 766: 284–290
 - 58 Dong S, Shen L, Li H, *et al.* Flexible sodium-ion pseudocapacitors based on 3D $Na_2Ti_3O_7$ nanosheet arrays/carbon textiles anodes. *Adv Funct Mater*, 2016, 26: 3703–3710
 - 59 Yin J, Qi L, Wang H. Sodium titanate nanotubes as negative electrode materials for sodium-ion capacitors. *ACS Appl Mater Interfaces*, 2012, 4: 2762–2768
 - 60 Dong S, Shen L, Li H, *et al.* Pseudocapacitive behaviours of $Na_2Ti_3O_7$ @CNT coaxial nanocables for high-performance sodium-ion capacitors. *J Mater Chem A*, 2015, 3: 21277–21283
 - 61 Dong S, Wu L, Wang J, *et al.* Self-supported electrodes of $Na_2Ti_3O_7$ nanoribbon array/graphene foam and graphene foam for quasi-solid-state Na-ion capacitors. *J Mater Chem A*, 2017, 5: 5806–5812
 - 62 Li H, Peng L, Zhu Y, *et al.* Achieving high-energy–high-power density in a flexible quasi-solid-state sodium ion capacitor. *Nano Lett*, 2016, 16: 5938–5943
 - 63 Qiu X, Zhang X, Fan LZ. *In situ* synthesis of a highly active $Na_2Ti_3O_7$ nanosheet on an activated carbon fiber as an anode for high-energy density supercapacitors. *J Mater Chem A*, 2018, 6: 16186–16195
 - 64 Wang C, Xi Y, Wang M, *et al.* Carbon-modified $Na_2Ti_3O_7 \cdot 2H_2O$ nanobelts as redox active materials for high-performance supercapacitor. *Nano Energy*, 2016, 28: 115–123
 - 65 Yang D, Sun X, Lim K, *et al.* Pre-sodiated nickel cobaltite for high-performance sodium-ion capacitors. *J Power Sources*, 2017, 362: 358–365
 - 66 Ding R, Qi L, Wang H. An investigation of spinel $NiCo_2O_4$ as anode for Na-ion capacitors. *Electrochim Acta*, 2013, 114: 726–735
 - 67 Wang YX, Chou SL, Wexler D, *et al.* High-performance sodium-ion batteries and sodium-ion pseudocapacitors based on MoS_2 /graphene composites. *Chem Eur J*, 2014, 20: 9607–9612
 - 68 Chauhan H, Singh MK, Kumar P, *et al.* Development of SnS_2 /RGO nanosheet composite for cost-effective aqueous hybrid supercapacitors. *Nanotechnology*, 2017, 28: 025401
 - 69 Wang R, Wang S, Peng X, *et al.* Elucidating the intercalation pseudocapacitance mechanism of MoS_2 -carbon monolayer interoverlapped superstructure: toward high-performance sodium-ion-based hybrid supercapacitor. *ACS Appl Mater Interfaces*, 2017, 9: 32745–32755
 - 70 Zhao C, Yu C, Zhang M, *et al.* Enhanced sodium storage capability enabled by super wide-interlayer-spacing MoS_2 integrated on carbon fibers. *Nano Energy*, 2017, 41: 66–74
 - 71 Niu F, Yang J, Wang N, *et al.* $MoSe_2$ -covered N,P-doped carbon nanosheets as a long-life and high-rate anode material for sodium-ion batteries. *Adv Funct Mater*, 2017, 27: 1700522
 - 72 Zhao X, Cai W, Yang Y, *et al.* $MoSe_2$ nanosheets perpendicularly grown on graphene with Mo–C bonding for sodium-ion capacitors. *Nano Energy*, 2018, 47: 224–234
 - 73 Xia Z, Sun H, He X, *et al.* *In situ* construction of $CoSe_2$ @vertical-oriented graphene arrays as self-supporting electrodes for sodium-ion capacitors and electrocatalytic oxygen evolution. *Nano Energy*, 2019, 60: 385–393
 - 74 Su Y, Zhitomirsky I. Asymmetric electrochemical supercapacitor, based on polypyrrole coated carbon nanotube electrodes. *Appl Energy*, 2015, 153: 48–55
 - 75 Su Y, Zhitomirsky I. Hybrid MnO_2 /carbon nanotube-VN/carbon nanotube supercapacitors. *J Power Sources*, 2014, 267: 235–242
 - 76 Dong J, Jiang Y, Li Q, *et al.* Pseudocapacitive titanium oxynitride mesoporous nanowires with iso-oriented nanocrystals for ultra-high-rate sodium ion hybrid capacitors. *J Mater Chem A*, 2017, 5: 10827–10835
 - 77 Zhu C, Yang P, Chao D, *et al.* All metal nitrides solid-state asymmetric supercapacitors. *Adv Mater*, 2015, 27: 4566–4571
 - 78 Dong S, Chen X, Gu L, *et al.* Facile preparation of mesoporous titanium nitride microspheres for electrochemical energy storage. *ACS Appl Mater Interfaces*, 2011, 3: 93–98
 - 79 Wang Q, Wen Z, Li J. A hybrid supercapacitor fabricated with a carbon nanotube cathode and a TiO_2 -B nanowire anode. *Adv Funct Mater*, 2006, 16: 2141–2146
 - 80 Xie X, Zhao MQ, Anasori B, *et al.* Porous heterostructured MXene/carbon nanotube composite paper with high volumetric capacity for sodium-based energy storage devices. *Nano Energy*, 2016, 26: 513–523
 - 81 Wang X, Kajiyama S, Iinuma H, *et al.* Pseudocapacitance of MXene nanosheets for high-power sodium-ion hybrid capacitors. *Nat Commun*, 2015, 6: 6544
 - 82 Kurra N, Alhabeb M, Maleski K, *et al.* Bistacked titanium carbide

- (MXene) anodes for hybrid sodium-ion capacitors. *ACS Energy Lett*, 2018, 3: 2094–2100
- 83 Chen S, Wu C, Shen L, *et al.* Challenges and perspectives for NASICON-type electrode materials for advanced sodium-ion batteries. *Adv Mater*, 2017, 29: 1700431
 - 84 Zhang S, Liu Y, Han Q, *et al.* Development and characterization of aqueous sodium-ion hybrid supercapacitor based on $\text{NaTi}_2(\text{PO}_4)_3$ /activated carbon. *J Alloys Compd*, 2017, 729: 850–857
 - 85 Phan TN, Gong MK, Thangavel R, *et al.* Ordered mesoporous carbon CMK-8 cathodes for high-power and long-cycle life sodium hybrid capacitors. *J Alloys Compd*, 2018, 743: 639–645
 - 86 Jian Z, Raju V, Li Z, *et al.* A high-power symmetric Na-ion pseudocapacitor. *Adv Funct Mater*, 2015, 25: 5778–5785
 - 87 Whitacre JF, Shanbhag S, Mohamed A, *et al.* A polyionic, large-format energy storage device using an aqueous electrolyte and thick-format composite $\text{NaTi}_2(\text{PO}_4)_3$ /activated carbon negative electrodes. *Energy Tech*, 2015, 3: 20–31
 - 88 Wei T, Yang G, Wang C. Iso-oriented $\text{NaTi}_2(\text{PO}_4)_3$ mesocrystals as anode material for high-energy and long-durability sodium-ion capacitor. *ACS Appl Mater Interfaces*, 2017, 9: 31861–31870
 - 89 Thangavel R, Kaliyappan K, Kang K, *et al.* Going beyond lithium hybrid capacitors: Proposing a new high-performing sodium hybrid capacitor system for next-generation hybrid vehicles made with bio-inspired activated carbon. *Adv Energy Mater*, 2016, 6: 1502199
 - 90 Thangavel R, Moorthy B, Kim DK, *et al.* Pushing the energy output and cyclability of sodium hybrid capacitors at high power to new limits. *Adv Energy Mater*, 2017, 7: 1602654
 - 91 Wang R, Lang J, Zhang P, *et al.* Fast and large lithium storage in 3D porous VN nanowires-graphene composite as a superior anode toward high-performance hybrid supercapacitors. *Adv Funct Mater*, 2015, 25: 2270–2278
 - 92 Karthikeyan K, Amaresh S, Kim KJ, *et al.* A high performance hybrid capacitor with $\text{Li}_2\text{CoPO}_4\text{F}$ cathode and activated carbon anode. *Nanoscale*, 2013, 5: 5958–5964
 - 93 Kaliyappan K, Amaresh S, Lee YS. LiMnBO_3 nanobeads as an innovative anode material for high power lithium ion capacitor applications. *ACS Appl Mater Interfaces*, 2014, 6: 11357–11367
 - 94 Du H, Yang H, Huang C, *et al.* Graphdiyne applied for lithium-ion capacitors displaying high power and energy densities. *Nano Energy*, 2016, 22: 615–622
 - 95 Lim E, Jo C, Kim H, *et al.* Facile synthesis of Nb_2O_5 @carbon core-shell nanocrystals with controlled crystalline structure for high-power anodes in hybrid supercapacitors. *ACS Nano*, 2015, 9: 7497–7505
 - 96 Kim H, Park KY, Hong J, *et al.* All-graphene-battery: bridging the gap between supercapacitors and lithium ion batteries. *Sci Rep*, 2014, 4: 5278
 - 97 Yuan Y, Wang C, Lei K, *et al.* Sodium-ion hybrid capacitor of high power and energy density. *ACS Cent Sci*, 2018, 4: 1261–1265
 - 98 Kim MS, Lim E, Kim S, *et al.* General synthesis of N-doped macroporous graphene-encapsulated mesoporous metal oxides and their application as new anode materials for sodium-ion hybrid supercapacitors. *Adv Funct Mater*, 2017, 27: 1603921
 - 99 Wasiński K, Półrolniczak P, Walkowiak M. Proof-of-concept study of a new type sodium-ion hybrid electrochemical capacitor with organic electrolyte. *Electrochim Acta*, 2018, 259: 850–854
 - 100 Fleischmann S, Widmaier M, Schreiber A, *et al.* High voltage asymmetric hybrid supercapacitors using lithium- and sodium-containing ionic liquids. *Energy Storage Mater*, 2019, 16: 391–399
 - 101 Wang F, Wang X, Chang Z, *et al.* A quasi-solid-state sodium-ion capacitor with high energy density. *Adv Mater*, 2015, 27: 6962–6968
 - 102 Ding J, Wang H, Li Z, *et al.* Peanut shell hybrid sodium ion capacitor with extreme energy–power rivals lithium ion capacitors. *Energy Environ Sci*, 2015, 8: 941–955
 - 103 Song MY, Kim NR, Cho SY, *et al.* Asymmetric energy storage devices based on surface-driven sodium-ion storage. *ACS Sustain Chem Eng*, 2017, 5: 616–624
 - 104 Wang P, Yang B, Zhang G, *et al.* Three-dimensional carbon framework as a promising anode material for high performance sodium ion storage devices. *Chem Eng J*, 2018, 353: 453–459
 - 105 Ajuria J, Redondo E, Arnaiz M, *et al.* Lithium and sodium ion capacitors with high energy and power densities based on carbons from recycled olive pits. *J Power Sources*, 2017, 359: 17–26
 - 106 Babu B, Shaijumon MM. High performance sodium-ion hybrid capacitor based on $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$ nanostructures. *J Power Sources*, 2017, 353: 85–94
 - 107 Cho SY, Yoon HJ, Kim NR, *et al.* Sodium-ion supercapacitors based on nanoporous pyroproteins containing redox-active heteroatoms. *J Power Sources*, 2016, 329: 536–545
 - 108 Ding J, Li Z, Cui K, *et al.* Heteroatom enhanced sodium ion capacity and rate capability in a hydrogel derived carbon give record performance in a hybrid ion capacitor. *Nano Energy*, 2016, 23: 129–137
 - 109 Phattharasupakun N, Wutthiprom J, Ma N, *et al.* Sodium-ion diffusion and charge transfer kinetics of sodium-ion hybrid capacitors using bio-derived hierarchical porous carbon. *Electrochim Acta*, 2018, 286: 55–64
 - 110 Yu F, Liu Z, Zhou R, *et al.* Pseudocapacitance contribution in boron-doped graphite sheets for anion storage enables high-performance sodium-ion capacitors. *Mater Horiz*, 2018, 5: 529–535
 - 111 Wang C, Wang F, Liu Z, *et al.* N-doped carbon hollow microspheres for metal-free quasi-solid-state full sodium-ion capacitors. *Nano Energy*, 2017, 41: 674–680
 - 112 Yang B, Chen J, Lei S, *et al.* Spontaneous growth of 3D framework carbon from sodium citrate for high energy- and power-density and long-life sodium-ion hybrid capacitors. *Adv Energy Mater*, 2018, 8: 1702409
 - 113 You Y, Wu XL, Yin YX, *et al.* High-quality Prussian blue crystals as superior cathode materials for room-temperature sodium-ion batteries. *Energy Environ Sci*, 2014, 7: 1643–1647
 - 114 Piernas-Muñoz MJ, Castillo-Martínez E, Gómez-Cámer JL, *et al.* Optimizing the electrolyte and binder composition for sodium Prussian blue, $\text{Na}_{1-x}\text{Fe}_{x+(1/3)}(\text{CN})_6 \cdot y\text{H}_2\text{O}$, as cathode in sodium ion batteries. *Electrochim Acta*, 2016, 200: 123–130
 - 115 Liu Y, Qiao Y, Zhang W, *et al.* Sodium storage in Na-rich $\text{Na}_x\text{Fe}(\text{CN})_6$ nanocubes. *Nano Energy*, 2015, 12: 386–393
 - 116 Xu Y, Zheng S, Tang H, *et al.* Prussian blue and its derivatives as electrode materials for electrochemical energy storage. *Energy Storage Mater*, 2017, 9: 11–30
 - 117 Lu K, Song B, Gao X, *et al.* High-energy cobalt hexacyanoferrate and carbon micro-spheres aqueous sodium-ion capacitors. *J Power Sources*, 2016, 303: 347–353
 - 118 Zhao F, Wang Y, Xu X, *et al.* Cobalt hexacyanoferrate nanoparticles as a high-rate and ultra-stable supercapacitor electrode material. *ACS Appl Mater Interfaces*, 2014, 6: 11007–11012
 - 119 Wang JG, Zhang Z, Zhang X, *et al.* Cation exchange formation of Prussian blue analogue submicroboxes for high-performance Na-

- ion hybrid supercapacitors. *Nano Energy*, 2017, 39: 647–653
- 120 Senthilkumar B, Sankar KV, Vasylychko L, *et al.* Synthesis and electrochemical performances of maricite- NaMPO_4 ($M = \text{Ni, Co, Mn}$) electrodes for hybrid supercapacitors. *RSC Adv*, 2014, 4: 53192–53200
- 121 Sundaram MM, Watcharatharapong T, Chakraborty S, *et al.* Synthesis, and crystal and electronic structure of sodium metal phosphate for use as a hybrid capacitor in non-aqueous electrolyte. *Dalton Trans*, 2015, 44: 20108–20120
- 122 Béguin F, Presser V, Balducci A, *et al.* Carbons and electrolytes for advanced supercapacitors. *Adv Mater*, 2014, 26: 2219–2251
- 123 Usui H, Domi Y, Shimizu M, *et al.* Niobium-doped titanium oxide anode and ionic liquid electrolyte for a safe sodium-ion battery. *J Power Sources*, 2016, 329: 428–431
- 124 Zhang Y, Nie P, Xu C, *et al.* High energy aqueous sodium-ion capacitor enabled by polyimide electrode and high-concentrated electrolyte. *Electrochim Acta*, 2018, 268: 512–519
- 125 Bae KL, Kim K. Flexible sodium-ion supercapacitor based on polypyrrole/carbon electrode by use of harmless aqueous electrolyte for wearable devices. *Int J Energy Res*, 2017, 41: 1335–1341
- 126 Xiong Q, Zheng C, Chi H, *et al.* Reconstruction of $\text{TiO}_2/\text{MnO}_2$ -C nanotube/nanoflake core/shell arrays as high-performance supercapacitor electrodes. *Nanotechnology*, 2017, 28: 055405
- 127 Lee J, Kim S, Kim C, *et al.* Hybrid capacitive deionization to enhance the desalination performance of capacitive techniques. *Energy Environ Sci*, 2014, 7: 3683–3689
- 128 Forsyth M, Yoon H, Chen F, *et al.* Novel Na^+ ion diffusion mechanism in mixed organic–inorganic ionic liquid electrolyte leading to high Na^+ transference number and stable, high rate electrochemical cycling of sodium cells. *J Phys Chem C*, 2016, 120: 4276–4286
- 129 Mendes TC, Zhou F, Barlow AJ, *et al.* An ionic liquid based sodium metal-hybrid supercapacitor-battery. *Sustain Energy Fuels*, 2018, 2: 763–771
- 130 Xu Z, Xie F, Wang J, *et al.* All-cellulose-based quasi-solid-state sodium-ion hybrid capacitors enabled by structural hierarchy. *Adv Funct Mater*, 2019, 334: 1903895
- 131 Wang Z, Li H, Tang Z, *et al.* Hydrogel electrolytes for flexible aqueous energy storage devices. *Adv Funct Mater*, 2018, 28: 1804560
- 132 Wang D, Li H, Liu Z, *et al.* A nanofibrillated cellulose/polyacrylamide electrolyte-based flexible and sewable high-performance Zn- MnO_2 battery with superior shear resistance. *Small*, 2018, 14: 1803978
- 133 González-Gil A, Palacin R, Batty P. Sustainable urban rail systems: Strategies and technologies for optimal management of regenerative braking energy. *Energy Convers Manage*, 2013, 75: 374–388

Acknowledgements This work was financially supported by the National Natural Science Foundation of China (51672308, 51972025 and 61888102).

Author contributions The paper was written with contributions from all authors. All authors have given approval to the final version of the paper.

Conflict of interest The authors declare that they have no conflict of interest.

Rui Jia received her BE degree in 2015 from Huaqiao University and ME degree in 2018 from Qingdao University. She is a PhD candidate at the College of Mathematics and Physics, University of Science and Technology Beijing. Her research interests mainly focus on sodium-ion batteries and hybrid supercapacitors.

Guozhen Shen received his BSc degree (1999) in chemistry from Anhui Normal University and PhD degree (2003) in chemistry from the University of Science and technology of China. He joined the Institute of Semiconductors, Chinese Academy of Sciences as a Professor in 2013. His current research focuses on flexible electronics and printable electronics, including transistors, photodetectors, sensors and flexible energy storage and conversion devices.

Di Chen received her BSc degree (1999) in chemistry from Anhui Normal University and PhD degree (2005) in chemistry from the University of Science and technology of China. She joined the University of Science and Technology Beijing as a Professor in 2014. Her current research focuses on energy storage materials and devices.

钠离子混合电容器的研究进展和未来展望

贾蕊¹, 沈国震^{2*}, 陈娣^{1*}

摘要 现代社会对电力系统和能源存储设备的能量密度、功率密度和工作寿命提出了更高的要求. 为了满足这一需求, 电池型负极和电容型正极组成的新型钠离子混合电容由于具有储备资源丰富和价格低廉的特点, 引起了人们的广泛关注. 值得一提的是, 钠离子混合电容在电池和超级电容器这两种储能方式之间起到了关键的桥梁作用, 使其在未来的大规模储能领域具有强大竞争力. 本文对电池型负极材料和电容型正极材料进行了细致的分类和介绍, 并对有机系电解质、水系电解质和离子液体电解质等多种电解质的特点进行了深入讨论. 此外, 我们对钠离子混合电容的应用现状及其在城市轨道交通中的潜在应用做了详细讨论. 最后, 分析了钠离子混合电容目前所面临的挑战, 并对其未来的发展方向作出了展望.