RESEARCH HIGHLIGHTS

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Recent progress and future prospect of novel multi-ion storage devices

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Rechargeable batteries, especially lithium-ion batteries (LIBs), have made rapid development since the 21st century, greatly facilitating people's lives[1–6]. Based on considerations of cost and existing problems (such as safety issues due to LIBs stacking strategy and unsatisfactory performance for various applications), researchers have explored alternative technologies to LIBs to meet the needs for wide application scenarios[5]. Among them, multi-ion storage devices such as dual-ion batteries (DIBs) and metal-ion hybrid capacitors (MIHCs) are considered promising alternative energy storage devices of LIBs due to their unique multi-ion storage mechanism. In a multi-ion storage device, cations and anions carry charges back and forth between the electrolyte and the electrodes at the same time, unlike the rocking chair mechanism of LIBs[7]. Generally, the anodes of DIBs and MIHCs work in a similar mechanism to LIBs, storing charge through redox reactions. The main difference among them is the mechanism of the cathodes during charging and discharging[8]. In DIBs, the battery-type cathode stores anions through the Faraday reaction. In MIHCs, the capacitive cathode usually stores anions through physical adsorption/desorption. These mean that two electrodes react with anions and cations respectively at the same time during charging and release both anions and cations back into the electrolyte simultaneously during discharging. The different energy storage mechanism of the cathodes makes the DIBs and MIHCs have different characteristics. Briefly, the high intercalation potential of the anion on the cathode makes the DIBs have a high working voltage, which is beneficial to obtain high energy density. Meanwhile, the adsorption/desorption behavior of anions on capacitive cathodes makes MIHCs can achieve a high power density. However, the similar energy storage mechanism of anode does not mean that the corresponding electrode materials and electrolyte system for metal-ion batteries can be applied directly to multi-ion storage devices. This is due to unsatisfactory electrochemical performance such as insufficient power density caused by kinetics mismatch. Therefore, the rational design and optimization of electrode materials and electrolyte systems are the key to the future development of multi-ion storage devices.

Anodes for multi-ion storage devices are currently the most investigated. And a shift has been made from material filtering to material optimization, to address the issues of kinetics mismatch and structural changes. Therefore, how to optimize electrode materials to obtain the best power performance without impairing the energy performance is the highlight and difficulty of current and future research. For this purpose, the nanoscale structure design is well known as one of the effective strategies for improving electrochemical performance and stability[9–11]. Typically, this method is usually combined with carbon material design to achieve a smaller size without agglomeration. Carbon-coated $Ba_{0.5}Ti_2(PO_4)_3$ nanospheres (BTP/C NSs) used as anodes of potassium ion hybrid capacitors (PIHCs) show excellent performance. When the power density is 129.1 W/kg, the maximum energy density of PIC can reach 566.1 W·h/kg, which is undoubtedly exciting. This anti-agglomeration strategy can also be further confirmed by Yang *et al.*[12]. They deposited two-dimensional MXene materials on a one-dimensional carbon nanotube (CNT). The prepared materials can effectively resist agglomeration. When used as an anode, the lithium-ion hybrid capacitor (LIHC) can achieve 201 W·h/kg high energy density at 210 W/kg power density. Even under the high-power density of 21 000 W/kg, the energy density can be kept at 92 W·h/kg. Beyond that, the composition control is also very impressive. By introducing heteroatoms into carbon materials and doping other atoms into materials, more active sites can be produced and better electrical conductivity can be achieved. Based on this principle, Te-doped MoS_2 nanosheets were prepared as a sample to confirm the optimization of the internal electronic structure of MoS_2 by introducing Te[13]. Meanwhile, the doped Te expanded the interlayer space and generated more active sites, facilitating performance. By comparing the TEM images of C@MoS_2 and C@$MoS_{2-x}Te_x$@C (Fig. 1(a)), it can be seen that Te doping inhibits the free growth of MoS_2, thereby significantly reducing the size of MoS_2 and facilitating the uniform distribution of nanosheets. As a result, Na-DIBs shows excellent cycle stability. At a current density of 1 A/g, it has a reversible capacity of 127.2 mA·h/g after 350 cycles, and the coulomb efficiency is as high as 98.9%. It

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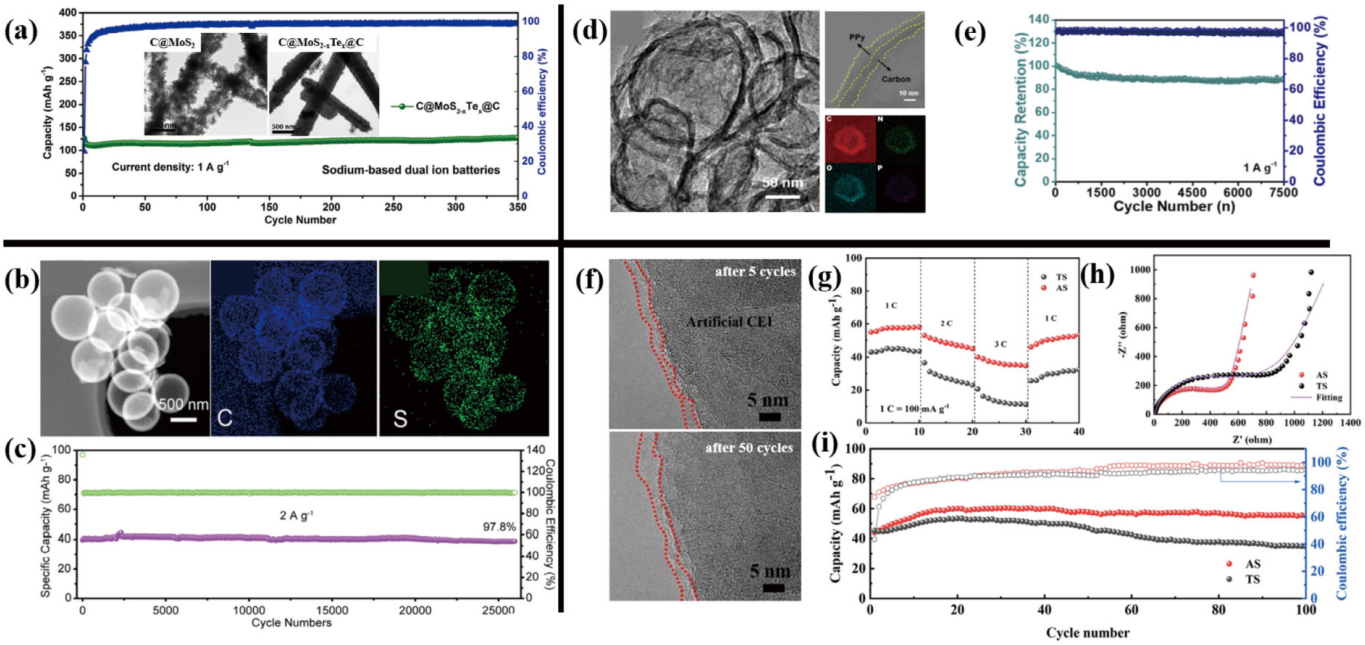

Fig. 1. (Color online) (a) Long-term cycle performance of C@$MoS_{2-x}Te_x$@C//graphite DIBs. Reproduced with permission[13], Copyright 2022, Elsevier. (b) EDS elemental mapping images of SHCS. (c) Cycling stability at 2 A/g of ACBC//SHCS PIHCs. Reproduced with permission[14], Copyright 2021, American Chemical Society. (d) EDS elemental mapping images of NPHCS@PPy. (e) Cycling performance at a current density of 1 A/g. Reproduced with permission[15], Copyright 2021, Frontiers. (f) TEM images of artificial CEI on graphite cathode after cycling after 5 cycles and 50 cycles. (g) Rate performance at different current density of AS and TS in KDIB. (h) Nyquist diagram. (i) Cycling performance of AS and TS. Reproduced with permission[16], Copyright 2022, Elsevier.

may be related to the optimized internal electronic structure, which improved reaction kinetics and increased active sites. For the introduction of heteroatoms in carbon materials, an attempt has been made to increase the content beyond the investigation of the mechanism of atomic effect mechanisms[14]. Superhigh sulfur-doped (6.8%) layered hollow carbon spheres (SHCS) with uniform size distribution were prepared (Fig. 1(b)). Due to the high sulfur content and reasonable structure, the PIHC has achieved a high-power density of 17.7 kW/kg at an energy density of 135.6 W·h/kg, and its cycle life at 2 A/g exceeds 26 000 times (Fig. 1(c)). Meanwhile, these two strategies are often used in combination. Zhang *et al.*[15] synthesized polypyrrole-coated N and P co-doped (Fig. 1(d)) hollow carbon nanospheres (NPHCS@PPy) as the anode of LIHCs. N and P atoms doped into the carbon lattice increase the degree of disorder and the distance between layers. In addition, N and P co-doping brings more structural defects, which helps to improve the accessibility of Li ions to active sites. Through the synergy of the two strategies, the LIHCs can provide 149 W·h/kg of high energy density and 22 500 W/kg of high-power density. Even after 7500 cycles, the capacity retention rate is 92% (Fig. 1(e)).

The behavior of the cathode largely determines the performance of the device. However, the research on the cathode is still in its early stage. Although the inherent high working voltage of DIBs is conducive to obtaining higher energy density, the excessive voltage will significantly accelerate the side reaction on the surface of cathode materials. As a result, the stability of the structure and cycling is severely undermined. Wang *et al.*[16] formed an artificial CEI film on the graphite electrode (Fig. 1(f)) to address this issue. The modified expanded graphite shows excellent anion storage capacity and cycle stability when used as the cathode of K-DIB. As shown in Fig. 1(g), the expanded graphite modified by artificial CEI (AS) shows better rate performance than pristine expanded graphite (TS) under the current density tests of 1 C, 2 C and 3 C, respectively. Under the current density of 1 C, the discharge capacity of 56.1 mA·h can be stably provided after 100 cycles. In addition, AS also shows lower resistance and better cycle stability than TS (Figs. 1(h) and 1(i)). This result confirms the feasibility and potential of cathodic surface modification. In addition, the activated carbon, which is widely used as the MIHCs cathode, makes the devices' energy density and practicability unsatisfactory[17]. Hence, an ordered-disordered hybrid carbon is reported as a cathode[18]. The much higher performance (with a specific capacity of 62.3 mA·h/g) than that of commercial activated carbon (17.6 mA·h/g) is due to such a unique mechanism of both anion adsorption and intercalation. When LIHC is assembled with the modified anode, the energy density reaches 231.5 W·h/kg at 0.05 A/g, and it can maintain 86.2 W·h/kg at 5.0 A/g even after 1000 cycles. Although great progress has been made in cathode materials for multi-ion storage devices, their specific capacity and structural stability are not enough for further application, and the investigation on cathode materials still needs to be continued.

In a multi-ion storage device, both cations and anions are used as carriers to transfer charges between the electrolyte and electrode. It means that the electrolyte can be considered both an ion transmission medium and an activated reaction material[19]. Hence, the electrolyte system has a significant impact on the performance of whole devices. In addition to improving the electrochemical stability window and increasing energy density, electrolytes can offer more possibilities for multi-ion storage devices. Recently, Chen *et al.*[20] de-

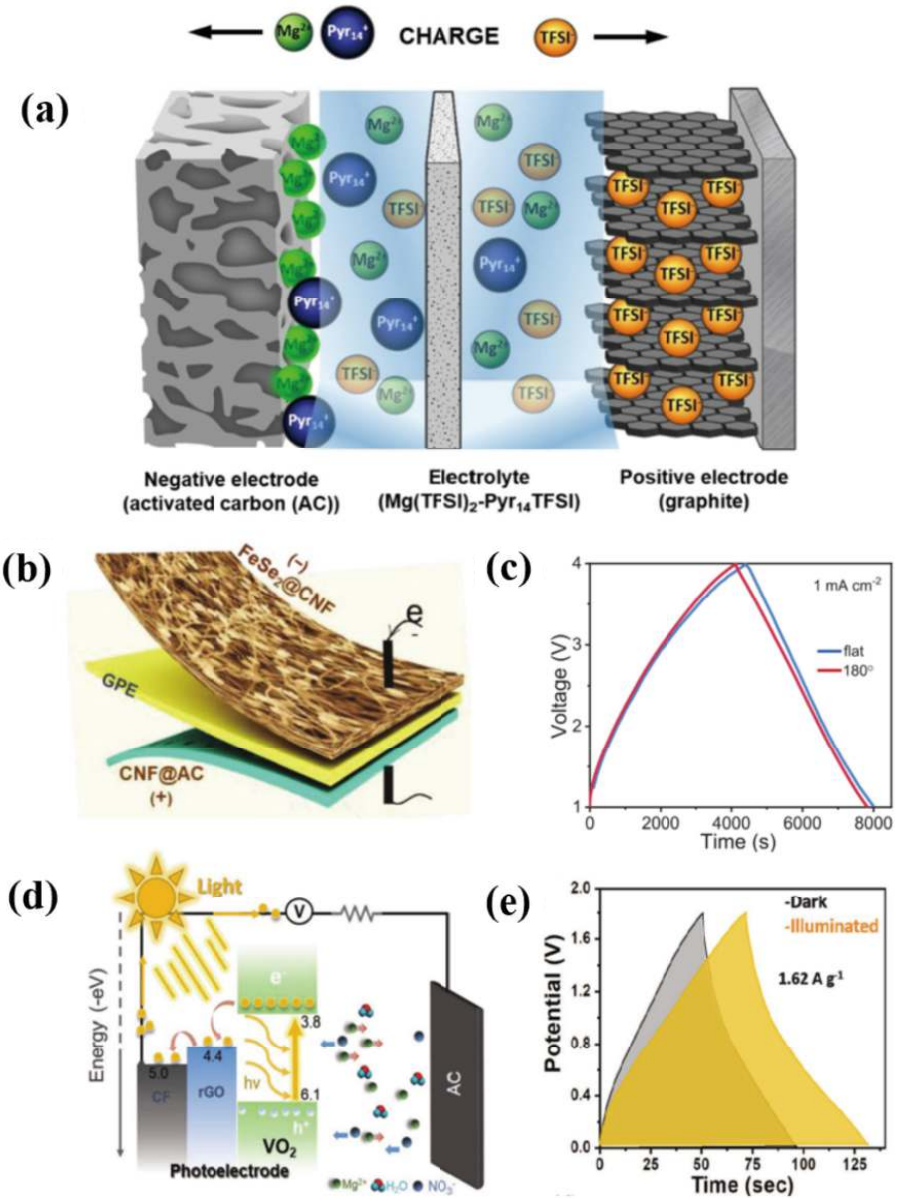

Fig. 2. (Color online) (a) Simplified illustration of the working principle of a dual-ion hybrid capacitor. Reproduced with permission[21], Copyright 2021, Elsevier. (b) Illustration of the bendable LIC device assembled with the $FeSe_2$@CNF anode, the CNF@AC cathode, and P(VDF-HFP)-based GPE. (c) GCD curve at the status of flat and bending for 180° of the obtained LIC. Reproduced with permission[22], Copyright 2022, Wiley. (d) Schematic illustration of the photocharging process of photo-MIC using VO_2/rGO photo electrode and AC counter electrode. (e) Galvanostatic measurements under dark and illuminated conditions (λ ≈ 455 nm, intensity ≈ 12 mW/cm^2) of photo-MICs at specific currents of 1.62 A/g. Reproduced with permission[23], Copyright 2022, Wiley.

veloped a new electrolyte, which uses lithium/sodium mixed organic solvent to achieve lithium insertion and sodium insertion at the same time. Li^+ and Na^+ can be inserted into $Li_4Ti_5O_{12}$ nanospheres at different potentials. The lithium/sodium hybrid ion capacitor using a mixed organic solvent system has a higher gravimetric energy density of 65.3 W·h/kg and good cycle efficiency (capacity retention rate of 3000 cycles is 95%), compared to single Li-MIHC or Na-MIHC. Meister *et al.*[21] reported a magnesium-based dual-ion MIHC, which realized simultaneous storage of multi-ions by adding $Mg(TFSI)_2$ to $Pyr_{14}TFSI$ electrolyte (Fig. 2(a)). During charging, Mg^{2+} and Pyr_{14}^+ cations are stored on the porous activated carbon anode through physical adsorption, and TFSI anions are inserted into the graphite cathode through the Faraday reaction. During discharge, ions are released back into the electrolyte. This strategy can also be extended to lithium-based dual-ion MIHCs. Future work can be focused on this promising direction to develop more dual-ion MIHCs.

Beyond the optimization of the device configuration, the functionalization of the device cannot be ignored in the future to suit more application situations. Recently, a flexible lithium-ion capacitor (LIC) has been developed to supply power to the wearable flexible human health monitoring sensor[22]. As shown in Fig. 2(b), this flexible LIC is composed of battery-type $FeSe_2$@CNF anode and capacitive-type CNF@AC cathode. Gel polymer electrolyte (GPE) is used as a separator and electrolyte. It shows long-term cycle stability (1100 cycles at 2 A/g) and impressive volume energy/power density (98.4 W·h/L at 157.1 W/L, 58.9 W·h/L at 15714.3 W/L). Even under the extreme conditions of 180° bending, there is still no obvious capacity attenuation, showing reliable mechanical flexibility (Fig. 2(c)). This result demonstrates the miniaturization

and flexibility of multi-ion storage devices. In addition, the devices can be also integrated with other functions such as solar energy conversion. Park *et al.*[23] prepared a light enhanced magnesium ion capacitor. A photocathode is composed of a mixture of VO_2 and reduced graphene oxide (Fig. 2(d)). When it is used to generate and separate photoelectric charges, light can be used to increase capacitance and rate performance. Fig. 2(e) shows the enhancement of capacitance when the device is illuminated. Combined with the previous work[2, 24–26], the electrochemical energy storage equipment driven by light has a huge application prospect, which can significantly reduce energy consumption in the future.

In a word, although still in its early stages, multi-ion storage devices have a promising future due to their unique advantages, such as the high operating voltage of DIBs and the high energy density/power density of MIHCs. This is because the demand for more applications is limited by the unsatisfactory performance exhibited by today's LIBs, especially for electric vehicles and grid-scale energy storage. The concept of this novel multi-ion storage device, which can provide both high energy and high power in a single device, is expected to meet the requirements of electric vehicles and smart grids. In addition, providing both high energy and high power in a single device also means that there are more application possibilities for highly lightweight and integrated designs. For example, benefiting from the ability to provide sufficient energy in highly integrated smart wearables or flexible energy storage devices, the application and development of flexible solid-state devices will be boosted. In addition, multi-ion storage devices offer significant economic and space efficiency compared to LIBs in harvesting recycled braking energy from trains and heavy vehicles. In order to realize its application early, we should design the device configuration rationally (including the optimization of electrodes and electrolytes). Meanwhile, we note that there are some promising design solutions such as devices with more ions involved in energy storage, and this direction deserves further research and development. Moreover, the functionalization of devices can be designed in parallel to cope with more application scenarios in the future.

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