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BRIEF OVERVIEW



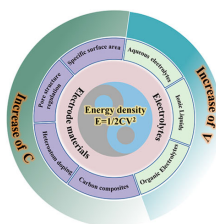
Unlocking the full energy densities of carbon-based supercapacitors

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ABSTRACT

Carbon-based supercapacitors (SCs) have limited energy density due to sluggish mass diffusion and restricted charge accumulation. To increase the energy density of carbon-based SCs, attention must be paid to the factors of specific capacitance and electrochemical stability window. This review summarizes recent signs of progress in carbon-based materials, including specific surface area, pore structure regulation, heteroatom doped, and carbon composites. In addition, we discuss aqueous, organic, and ionic liquid electrolytes that affect the electrochemical stability window of SCs. Finally, the possibilities for achieving synergy in electrode/electrolytes are summarized via enhancing the pseudocapacitance contribution and developing high-voltage window electrolytes.



IMPACT STATEMENT

Based on the latest research progress of carbon-based supercapacitors, this paper aims to provide new insights and guidance on improving energy density from delicate architecture of electrode materials and electrolytes.

ARTICLE HISTORY

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KEYWORDS

Carbon-based supercapacitors; energy density; electrode materials; electrolytes

1. Introduction

As an important branch of energy storage and system, electrochemical energy storage devices (EES) play an important role in the development of the national economy. EES are referred to as various types of batteries and supercapacitors (SCs) [1–5]. The current lithium-ion batteries (LIBs) orientated technology platform does not meet the requirements of high-power applications [6–8]. There is a strong demand for energy storage technologies suited for concurrently high energy density (E_d) and high power density (P_d) applications [9]. SCs are considered to be highly promising next-generation high-power EES due to their high P_d , good rate performance, long

cycle life, fast charging/discharging speed, and excellent safety. Tremendous attention has been attracted in recent years [10–12]. However, a key issue that needs to be tackled is their E_d much lower than that of LIBs and fuel cells, usually only reaching about one-tenth of the latter, so the development and commercial application of SCs has been seriously restricted [13,14].

As the conventional electrode material used in SCs, carbon materials have unique physical and chemical properties: high specific surface area (SSA), low density, high stability, excellent electrical conductivity, regulated pore structure, excellent corrosion resistance, and low price [15–17]. Carbon-based SCs are a promising

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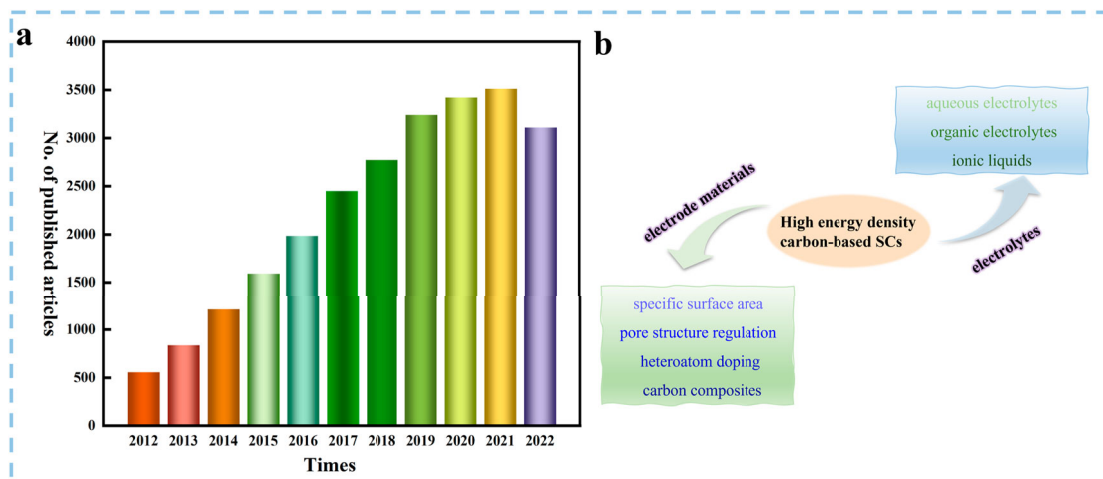


Figure 1. (a) Trends in the number of publications on carbon-based SCs (Source: Web of Science, December 31, 2022). (b) Energy density enhancement strategies for carbon-based supercapacitors.

high-power device with great commercial market potential, offering fascinating characteristics such as fast energy pulses, good charge/discharge cycle performance, wide operating temperature and high coulombic efficiency [18–20]. Figure 1(a) shows the development history of carbon-based SCs from 2012 to 2022, and the relevant publication has increased by ~ 6 times in the past ten years. However, SCs using carbon materials have still suffered from low E_d (< 10 Wh/kg) due to slow mass diffusion and limited charge accumulation. To solve this problem, we must tackle from the formula:

$$E = \frac{CV^2}{2} \quad (1)$$

A lot of work has been put into developing large-capacitance (C) electrodes and high-potential (V) electrolytes as two key components that can increase the energy density (E) of carbon-based SCs [21,22]. The increase in specific capacitance (S_c) can be achieved through the appropriate design of SSA, pore structure regulation, heteroatom doping, and carbon composites, while the electrochemical stability window (ESW) of the device is defined by the choice of electrolyte (Figure 1(b)) [23,24].

We review the recent progress of high E_d carbon-based SCs. First, the development history and three mechanisms of SCs are briefly introduced. Then, research on carbon-based electrodes for SCs in recent years is summarized, including SSA, pore structure regulation, heteroatom doping, and carbon composites. In addition, aqueous, organic and ionic liquid electrolytes that affect the ESW of carbon-based SCs are discussed. Finally, we propose the future direction of developing electrode/electrolyte synergy in high E_d carbon-based SCs

by improving the pseudocapacitance contribution and developing high ESW electrolytes.

2. History and mechanism of supercapacitors

2.1. Previous generation and this life

As early as ancient Greece, it was discovered that rubbing amber with cloth could attract light objects, which was attributed to the fact that friction causes the amber to become electrically charged, thus making the dielectric charges mechanically separated. In 1745, the first capacitor in history was invented: the Leiden jar, which consisted of a glass container, the inner and outer surfaces were laminated with metal foil, and the metal foil and glass were used as electrodes and dielectrics, respectively [25]. In 1853, the German physicist Hermann von Helmholtz first introduced the concept of double-layer capacitance [26]. In 1957, General Electric was granted the first patent for the invention of an electrochemical capacitor device, proposing a double-layer system with porous carbon as the electrode and sulfuric acid as the electrolyte, opening a new chapter in the rapid development of the field [27]. In 1979, NEC introduced the first commercially successful double-layer capacitor, named the ‘supercapacitor’, a major step forward in the history of supercapacitors [28]. By the 1980s, many companies were producing electrochemical capacitors designed for applications such as electric cars, medical devices, and military applications. In the twenty-first century, with the rapid development of the electric vehicle industry, supercapacitors have become a significant research hotspot for new energy storage devices worldwide. With the advantages of good rate capability, excellent safety, fast charge/discharge, long cycle life, and high P_d , supercapacitors play a significant part in the field of EES

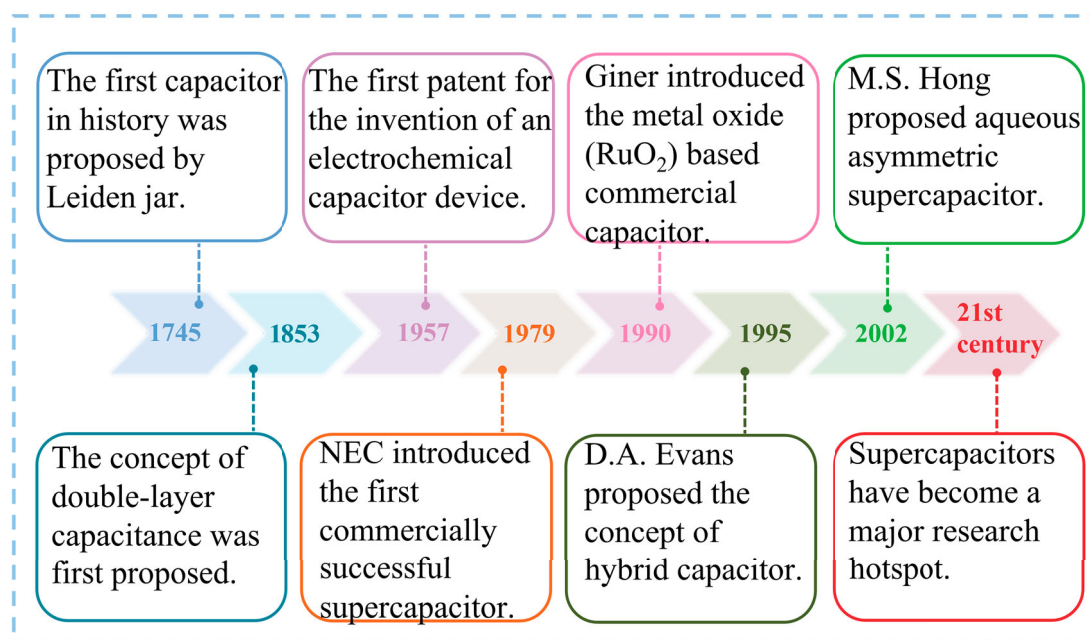


Figure 2. Development history of supercapacitors.

technology. It was the continuous research breakthroughs in these areas that ushered in the dawn of supercapacitors toward commercial applications (Figure 2).

2.2. Working mechanism

2.2.1. Electric double-layer capacitors

The main energy storage mechanism of the electric double-layer capacitor (EDLC) lies at the reversible electrostatic accumulation of ions on the porous carbon surface [29]. Excessive or insufficient charges build up on the electrode surface in the contact between the carbon particles and the electrolyte. To ensure electrical neutrality, electrolyte ions with charge balancing function continuously travel through the electrolyte, and eventually charge accumulation takes place on the electrode side and forms a cohesive layer, called the electric double layer [30,31].

In the external circuit, electrons go from positive to negative during charging, while cations migrate to the negative electrode and anions to the positive electrode to balance the charge. In contrast, during discharge, the electrons move in the exact opposite direction (Figure 3(a)). The presence of the electrolyte only transfers ions for the electrode material and the whole process is not involved in the reaction. Therefore, the EDLC is a purely physical process, with no expansion of the electrode material during charging and discharging. This storage mechanism allows ultrafast energy absorption and transport during millions of charging/discharging cycles, and the EDLC thus exhibits high stability [32].

2.2.2. Pseudocapacitors

The charge storage mechanism of pseudocapacitors is the Faradaic process, which involves charge transfer between the electrolyte and the electrode material, resulting in a fast and reversible redox reaction [33]. When a voltage is applied to the capacitor, the pseudocapacitive material produces the same electrical response as the EDLC, and the proportionality constant resulting from the continuous change of the state of charge with the potential is called capacitance. Pseudocapacitors can be divided into three main categories: (1) underpotential deposition, (2) redox pseudocapacitors and (3) intercalation pseudocapacitors (Figure 3(b)) [34].

Underpotential deposition is an electrodeposition phenomenon. Specifically, when the electrode potential is higher than the thermodynamic equilibrium potential of the metal cation A in the electrolyte, the metal cation will be reduced and deposited as a solid metal on the surface of the substrate B [35]. This process is usually attributed to the strong interaction of the electrodeposited metal A with substrate B, and this A-B interaction needs to be energetically stronger than the A-A interaction. It is worth mentioning that the deposition process of surface coatings can be precisely and efficiently controlled by underpotential deposition, which has a good potential for the study of properties related to metal/forged layer composites, their microstructures and their electronic properties [36]. Redox pseudocapacitance refers to the Faradaic charge transfer behavior that accompanies when ions are electrochemically adsorbed at the surface of a material. During the charging and discharging process,

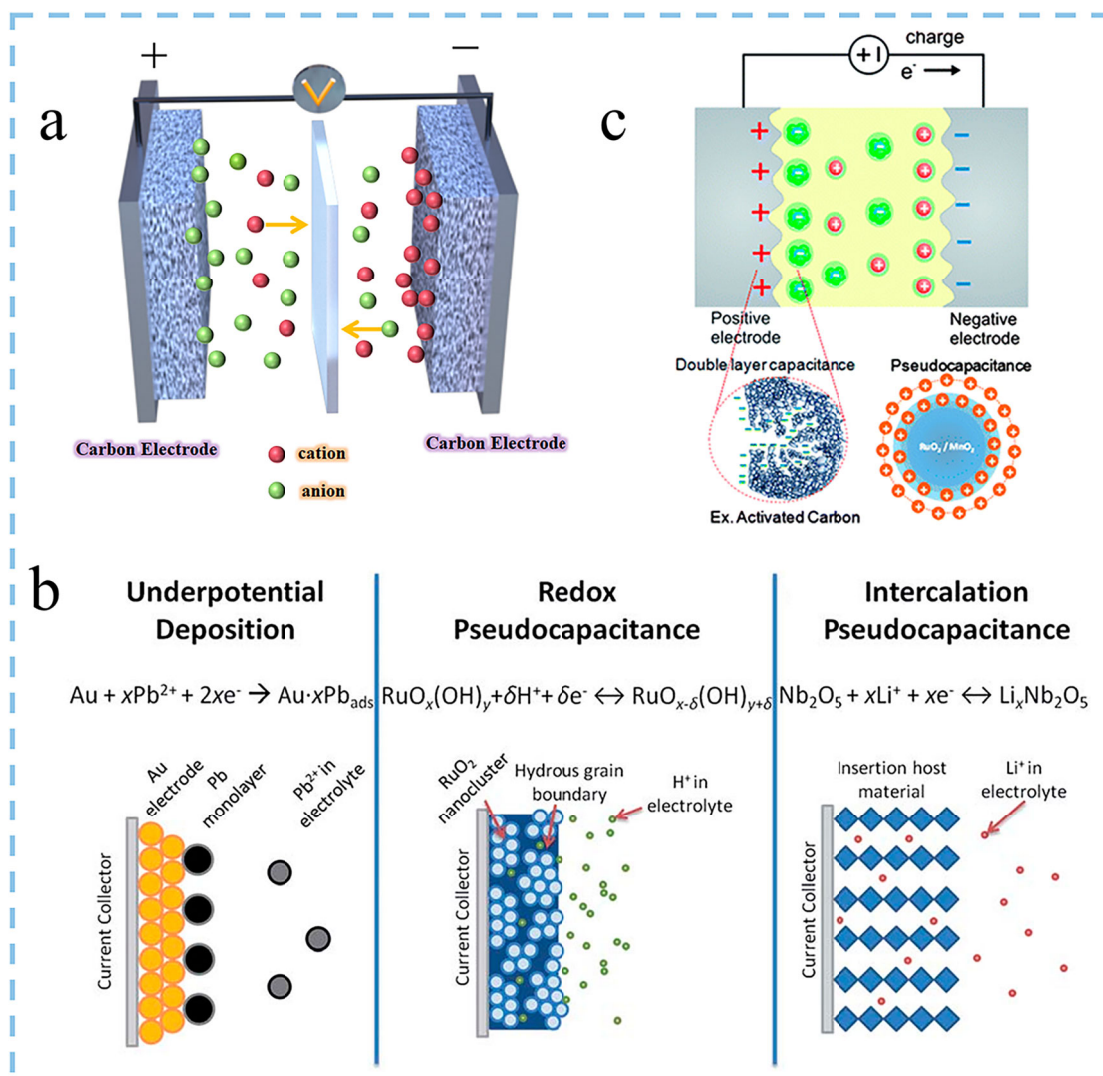


Figure 3. (a) Energy storage mechanism of electric double-layer supercapacitors. (b) Different types of reversible redox mechanisms that give rise to pseudocapacitance [34]. Copyright 2014, The Royal society of chemistry. (c) Schematic diagram of the charging and discharging process of hybrid capacitor [47]. Copyright 2011, The Royal society of chemistry.

a reversible functionalized molecular layer is formed on the electrode surface [37,38]. Intercalation pseudocapacitance involves the conduction of ions within the matrix material or the rapid diffusion between layers, and unlike the intercalation behavior of batteries, no phase transition occurs in this process [39]. At present, the systems involving intercalation pseudocapacitance mainly include intercalation of Li⁺ or H⁺ into the pores or layers of some transition metal compounds such as TiO₂, MoS₂ and T-Nb₂O₅ [40–42]. In addition, for transition metal carbides (MXene), cations with larger radii (Na⁺, K⁺, NH₄⁺, Al³⁺, etc.) can also complete the intercalation pseudocapacitance process [43,44].

2.2.3. Hybrid capacitors

In asymmetric capacitors, two electrodes have two different charge storage mechanisms, including capacitive

and faraday battery, which provides a feasible alternative to traditional double-layer capacitors and pseudocapacitors. Asymmetric capacitors combine the larger capacitance of pseudocapacitors with the better power performance and cycle stability of double-layer capacitors [45]. When correctly matched positive and negative electrodes are combined in the same capacitor, the voltage window can be improved, as well as the power and energy density of the capacitor [46].

In addition, attempts have been made to make hybrid capacitors that combine capacitive and battery capacitors, in which one pole of an asymmetric supercapacitor is replaced with the electrode material of a secondary battery. The device can be charged and discharged in a short time and under a large current, which is suitable for the start-up of currently popular hybrid electric vehicles (Figure 3(c)) [47].

3. Electrode materials

The performance of SCs is greatest impacted by the electrode material of all the variables. Three categories of electrode materials are available for SCs [48]: carbon materials, metal oxides/hydroxides, and conducting polymers. In SCs, carbon-based materials are the most extensively researched and used, providing the following advantages [49,50]: (1) favorable availability, (2) promoted affordability, (3) good electrical conductivity, (4) non-toxicity, (5) ease of manufacture, (6) strong mechanical qualities, (7) high chemical stability, (8) increased SSA, and (9) wide working temperature range. It is well known that carbon materials with high S_c have made more and more significant breakthroughs in recent years, among which the regulatory structure engineering of carbon materials has been an important means to obtain high E_d .

3.1. Specific surface area

SCs are significantly impacted by carbon materials with high SSA and carefully regulated distribution of pore sizes. When carbon-based SCs are being charged, the oppositely polarized electrodes acquire equal quantities of positive and negative charges. The simultaneous adsorption and desorption of electrolyte ions maintain the electrical neutrality of electrode/electrolyte contacts. Because of the highly disordered nature of the electrode materials in current carbon-based SCs, the EDLC model is unable to accurately describe the capacitive behavior of these devices. The capacitance of EDLC is given by [51]:

$$C = \frac{\varepsilon_0 \varepsilon_r A}{d} \quad (2)$$

where C is the capacitance (F), ε_0 is the permittivity of the vacuum, ε_r is the proportional permittivity of the electrolyte, A is the area that can be accessed by ions of the electrode material, and d is the effective thickness of the double layer. It is evident from this formula, nevertheless, that the S_c is heavily reliant on the ion-available surface for the production of EDLC [52,53]. Thus, increasing the SSA of carbon materials is one of the most crucial elements to enhance the S_c of carbon-based SCs.

From the aforementioned, it appears that a large SSA is preferred to produce significant capacitance in carbon-based electrodes. The SSA is mainly provided by the pore structure of carbons, which plays a key role in providing an extensive accumulation space for high-energy storage [54–56]. Therefore, carbons with perfect pore structures have attracted much scientific interest in the field of SCs electrodes. These materials are usually carbon-rich precursors pre-carbonized and activated to produce

microporous structures. Chemical activation generally uses chemicals such as KOH, NaOH, H_3PO_4 , $ZnCl_2$, and K_2FeO_4 for heat treatment of electrode materials. While physical activation is carried out in a high-temperature oxidizing atmosphere (such as carbon dioxide, oxygen, or steam) at 700–1200°C [57,58]. A large number of studies have focused on potassium salt, and chemical activation is usually accompanied by the redox reaction between potassium salt and carbon materials at high temperatures. KOH is a highly corrosive salt, which is most commonly used in activation. Sun et al. [59] reported a nitrogen-doped hierarchical porous carbon (NHPC) by pre-carbonization of silkworm cocoons and subsequent KOH activation, with a SSA up to 3386 m²/g and a volume ratio of mesopores and macropores of about 45.5%. The resulting NHPC has a high SSA, high defect density, hierarchical porosity, and a relatively high volumetric proportion of mesopores and macropores. These properties not only provide a large number of active sites for charge storage, but also make it easier for the electrolyte ions to move between the electrodes. The E_d of the SCs in the organic electrolyte is 34.41 Wh/kg, while the P_d is 31.25 kW/kg. Mixed activation of KOH and other salts induces both porosity and graphitized structures in porous carbon. Yang et al. [60] reported a porous carbon with phoenix fruit as the carbon source and KOH activator, which has a regulated pore size distribution, an extremely large SSA (3463 m²/g), and an interconnected pore structure (Figure 4(a,b)). The interconnected macropores build a system of cross-linked tubular channels in the obtained samples, which act as a ‘highway system’ for the rapid transport of electrolyte ions to the terminal mesopores and micropores. The interconnected macropores and mesopores mainly inherit the well-developed tubular water transport system in Phoenix fruit, while the micropores are produced by the etching of the pore walls of the macropores and mesopores by KOH.

In another example, Gao et al. [61] reported an electrode material with $C_3N_3Na_3S_3$ /KOH as dual activators and egg yolk as precursors. The authors propose the definition of S_{micro}/S_{BET} to reflect the structure-function relationship, which improves the selectivity of high-performance supercapacitor electrode materials. By adjusting the mass ratio of $C_3N_3Na_3S_3$ /KOH, S_{micro}/S_{BET} varied from 74.69% to 26.26% and the SSA was 3519.50 m²/g. Yao et al. [62] reported a two-dimensional hierarchical porous carbon nanosheet (2D-HPC) with high scalability. 2D-HPC was prepared by mixing phenylenediamine-acetaldehyde (PDAA) with KOH powder at 800°C under N_2 atmosphere for 2 h. The high flexibility, large SAA and layered porosity, together with the turbine layer microstructure and nitrogen

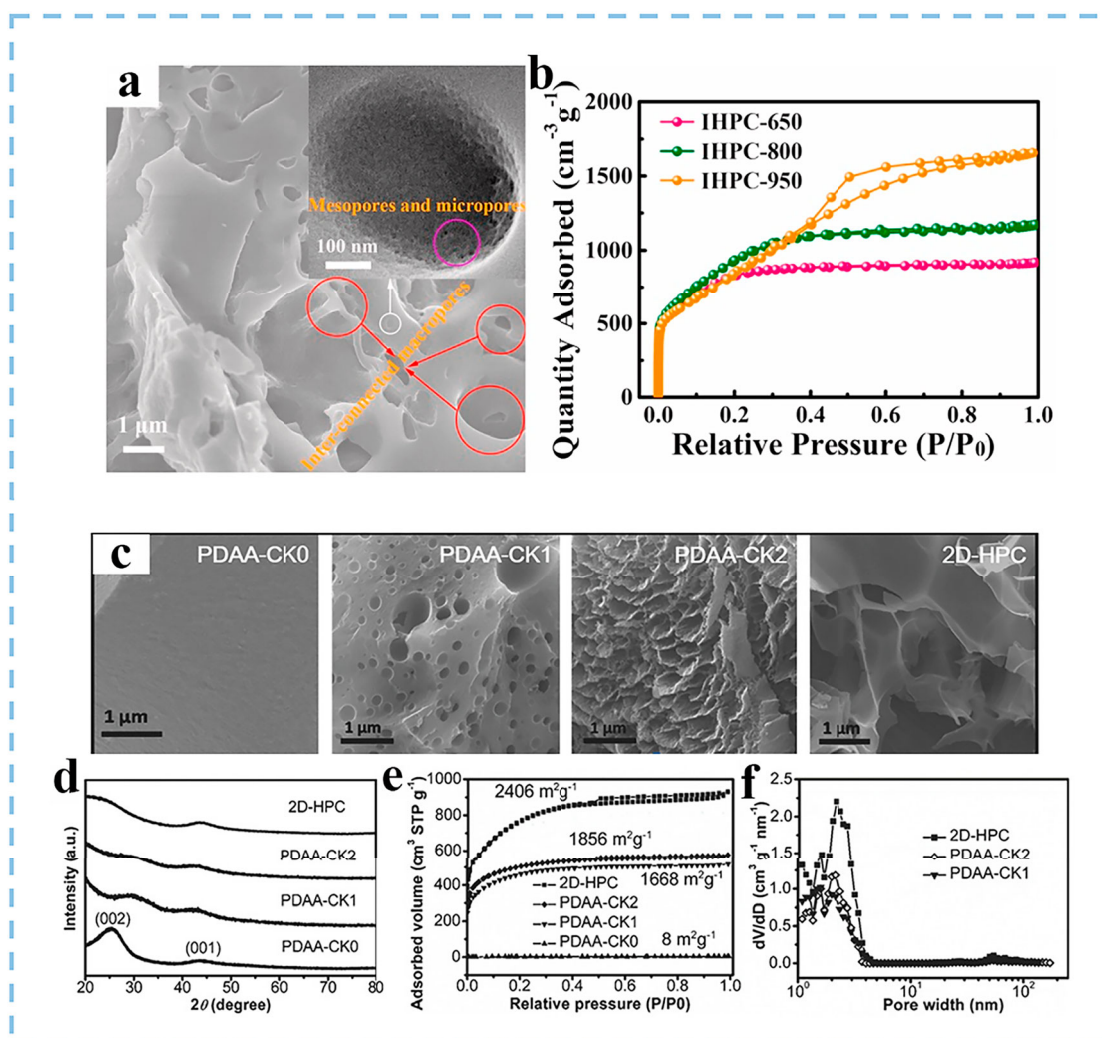


Figure 4. (a) SEM image of the typical sample IHPC-800. (b) Nitrogen adsorption/desorption isotherms of the obtained samples [60]. Copyright 2021, Elsevier. (c) The SEM images of the resultant carbons are shown. (d) XRD patterns of PDAA-derived carbons. (e) N₂ adsorption-desorption curves and (f) pore size distribution for the PDAA-derived carbons [62]. Copyright 2018, Wiley-VCH.

dopants, make 2D-HPC an ideal material for flexible energy storage. 2D-HPC is typically 1.5 nm thick, 1–3 μm wide, has a high SSA (2406 m²/g) (Figure 4(c–f)). Assembled into symmetric SCs, the E_d is 139 Wh/kg, and it exhibits excellent cycling stability.

3.2. Pore structure regulation

For SCs, a large surface area is always ideal only the surface of electrode material accessible to electrolyte ions can contribute to charge storage. Therefore, it is crucial that the electrolyte and electrode materials match well. The pore size has a substantial effect on the mobility of electrolyte ions into the pores of electrode material. If the pore size of the electrode material is too small, the ions cannot enter and there is no contribution to the double-layer capacitance. If the pore size of the electrode material is too large, there is no contact with the electrolyte ions,

which is also not helpful to the charge storage, so the SSA of the electrode material and the S_c of the SCs are not linear [63]. An excessive increase in the SSA leads to a decrease in mesoporosity, a decrease in carrier density, and an increase in pore volume, which reduces the charge storage capacity. Furthermore, the surface area calculated depending on the use of density-functional theory (DFT) exceeds 1200 m²/g and the S_c becomes saturated [64]. When the porosity exceeds a certain level, the S_c of nanocarbon decreases. In addition, the higher SSA reduces the bulk capacitance of the SCs electrodes and lowers the P_d [65].

In 1985, three types of pores were identified by the International Union of Pure and Applied Chemistry (IUPAC) based on their diameters: micropore (< 2 nm), mesopore (2 ~ 50 nm), and macropore (> 50 nm) [66]. IUPAC redefined its classification in 2015, introducing three new pore types [67]: Nanopores (< 100 nm),

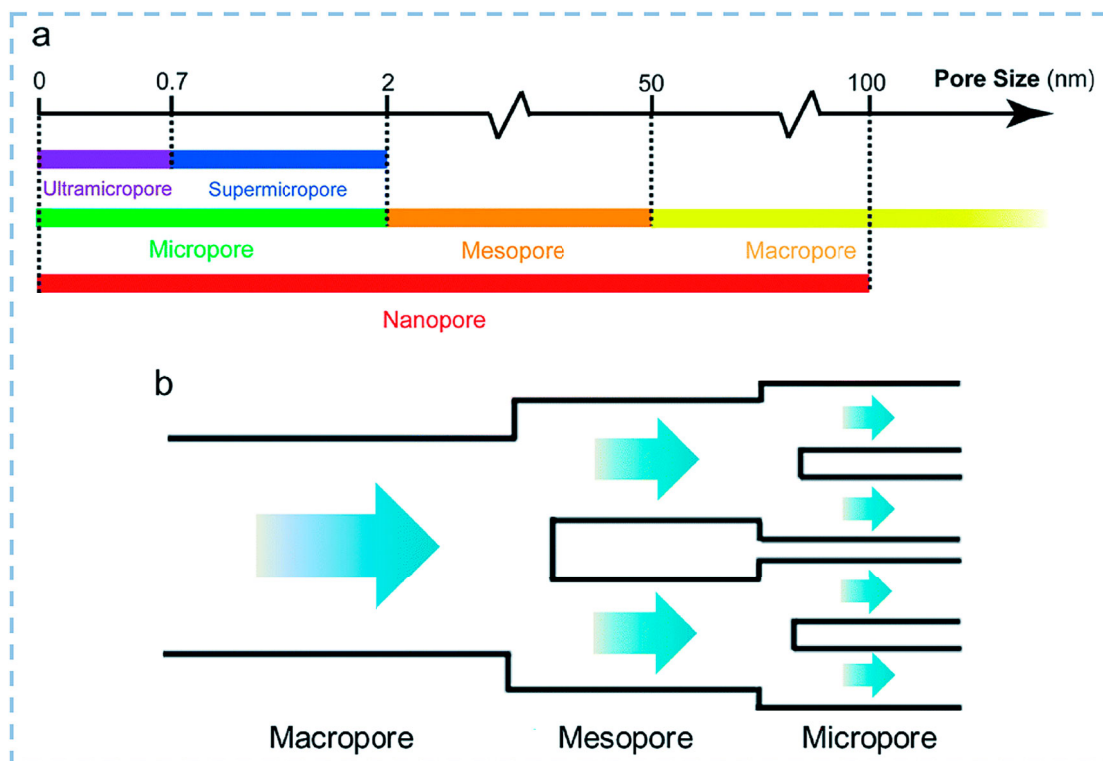


Figure 5. (a) IUPAC classifications of pores based on the pore width. (b) Schematic illustration of an ion diffusion pattern in a typical hierarchical porous structure [68]. Copyright 2017, The Royal society of chemistry.

Supermicropores (0.7 ~ 2 nm), and Ultramicropores (< 0.7 nm). According to the new definition, nanopores (< 100 nm) are classified as micropores, mesopores and macropores. Micropores include supermicropores and ultramicropores. The classification of pore types is summarized in Figure 5(a) [68]. Figure 5(b) shows the transport paths of ions in the porous structure: ions enter through the larger pores and then flow sequentially into the smaller ones. This process keeps going until the ions get to the tiniest pores. To completely use the carbon surface, the pore size of the carbon material can be properly adjusted to transport enough electrolyte ions across the electrode [69]. Microporous charge accumulation by molecular diffusion, while mesopores/macropores serve as a shortcut for ion diffusion to shorten the transport route and decrease the interfacial resistance of the electrolyte [32]. Furthermore, the hierarchical porous structure comprised of interconnected micropores, mesopores, and macropores is of particular interest for high-performance SCs, considering the synergistic effect between the numerous micropores as ion adsorption sites and the interconnected mesopores/macropores, which ensures fast ion transport and remarkably achieves a mutual enhancement of E_d/P_d [70,71]. As a result, extensive study into the pore structure and surface morphology of carbon-based materials has begun.

Template technology is an important method to efficiently fabricate porous carbons with high SSA and well-regulated pore size distribution [72,73]. Template approaches can be divided into hard-templates, soft-templates, and self-templates based on various synthesis processes. To achieve integral control over the pore-size distribution, the hard/soft-templating methods can be modified to create hierarchical porous carbons [74]. Various porous template carbons for high-performance SCs were prepared by using these methods.

3.2.1. Hard-templates

The hard template method is also known as the nanocasting method. It involves mixing a template with a carbon precursor to form a complex of the two, and finally obtaining a carbon product with the same structure as the template by carbonization and removal of the template. To create uniformly porous structures, hard templates including MgO, CaCO₃, NaNO₃, Fe₂O₃, SiO₂, and KCl were frequently utilized [75]. As a commonly used hard template, CaCO₃ decomposes to form calcium oxide particles and carbon dioxide gas at a temperature of 500°C. The generated carbon dioxide gas escapes to generate micropores, and after the removal of calcium oxide, the micropores merge to form mesopores and macropores, forming a layered porous carbon material. Li et al. [76] reported a corn stover porous carbon with potassium

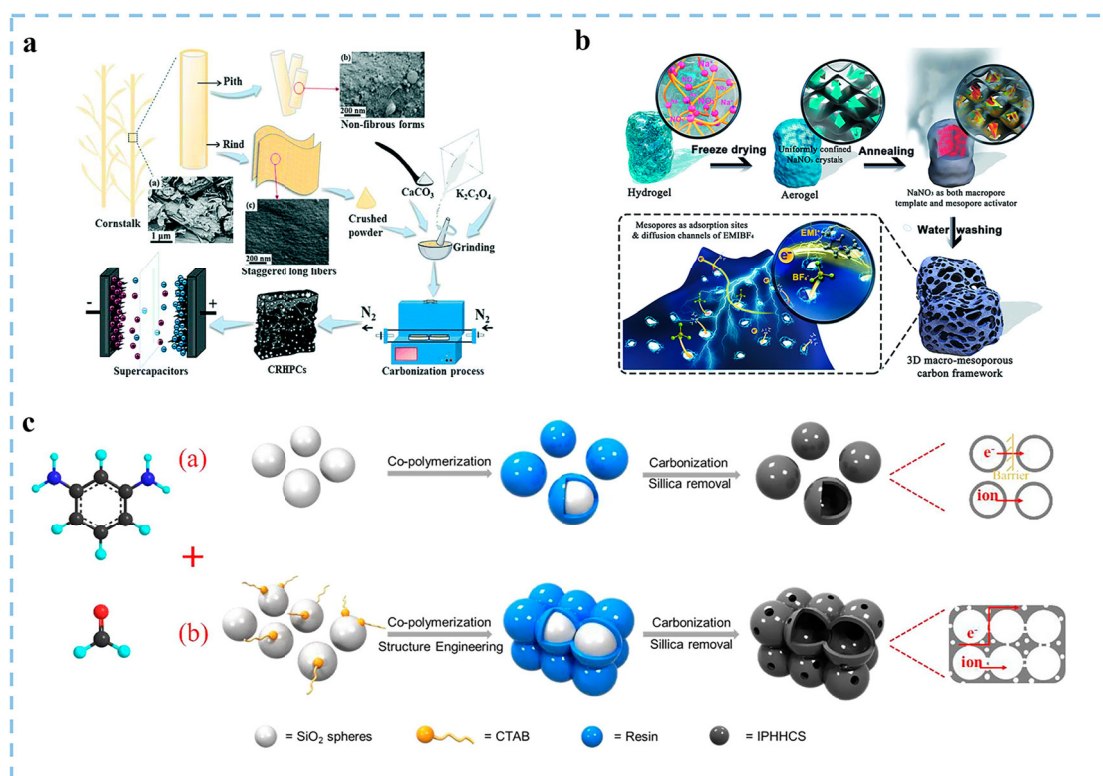


Figure 6. (a) Schematic fabrication process of the HPCs from cornstalk rind in a one-pot manner [76]. Copyright 2020, The Royal society of chemistry. (b) The synthesis schematic illustration of 3D cross-coupled macro-mesoporous carbon electrode via NaNO_3 template strategy [77]. Copyright 2018, Wiley-VCH. (c) Schematic illustration of the fabrication of MHCs with SiO_2 spheres and IPHHCSs with SiO_2 spheres and CTAB [78]. Copyright 2021, Elsevier.

oxalate as an activator, using CaCO_3 as a hard template to facilitate the activation process and tune the pore size distribution (Figure 6(a)). The increased mesoporosity and graphitization degree of carbon materials provide good performance for SCs. The SCs exhibit a high S_c of 461 F/g at 0.5 A/g. Meanwhile, it exhibits good cycling stability with high capacitance retention of 90.4% after 10000 cycles. In addition, the SCs show a high E_d of 42.5 Wh/kg at a P_d of 0.4 kW/kg. Li et al. [77] used NaNO_3 as a hard template, decomposed at 600 °C to generate microporous/mesoporous structures (Figure 6(b)). Gelatin as a carbon source can gelatinize and NaNO_3 as a hard template and activator can decompose into N_2 , O_2 and NO . The gas release process produces a swelling effect and expands the pore size to 2–4 nm. High SSA, 3D interconnected N-doped carbons were prepared without adding other N sources. The SCs achieved a high E_d of 92 Wh/kg at a P_d of 1 kW/kg in EMIBF₄ electrolyte. Cheng et al. [78] used the SiO_2 hard templating route to prepare interconnected porous carbon spheres (IPHHCSs) with high SSA, high mesoporosity, and high heteroatom doping rate (Figure 6(c)). For comparison, mutual-isolated hollow carbon spheres (MHCs) were prepared without structure design. IPHHCSs have low interfacial resistance between the spheres, a large number of locations

for ion storage, and the presence of pathways for fast ion diffusion in mesopores. The electrodes of the SCs provide a high S_c of 295 F/g at 1 A/g, while the capacitance retention can reach 87% at 20 A/g with high cycle life stability (98.8% after 10000 cycles). Du et al. [79] achieved large mesopore size by encapsulating mesoporous polymer spheres in a dense silica shell for pyrolysis. Increasing the amount of SiO_2 precursor enlarges the pore size of ordered mesoporous carbon spheres (O-MCS) from 3.1 ~ 10.0 nm and the SSA from 696 to 1186 m²/g.

3.2.2. Soft-templates

Unlike hard templates, which have a solid rigid structure, soft template materials are mainly copolymers or organic molecules. These soft templates generally cluster in a self-assembled manner into charged and hydrophilic template clusters, which can bind to carbon source precursors through electrostatic interactions [80]. Carbon/organic complexes are formed by copolymerization and bonding between carbon precursors and soft templates through covalent bonds, and the resulting complexes are finally carbonized in a high-temperature inert atmosphere. One of the most prominent advantages of the soft template over the hard template method is that

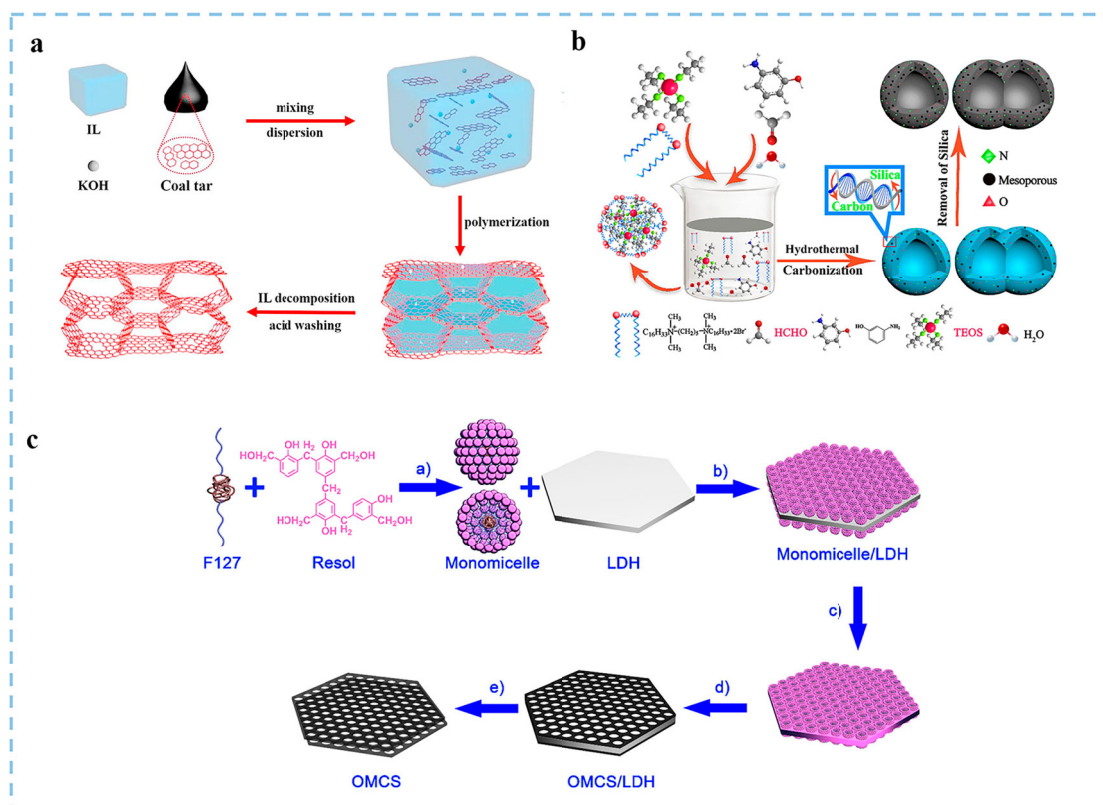


Figure 7. (a) Schematic illustration of the synthesis process of ISPCs [82]. Copyright 2018, Elsevier. (b) Synthesis of Nitrogen-doped polymer-silica and carbon-silica composite nanospheres with cross-interlocking mesostructures [83]. Copyright 2020, Elsevier. (c) Schematic illustration of the fabrication process for the OMCSs [84]. Copyright 2018, American Chemical Society.

it avoids removing the template material after carbonization, simplifying the experimental steps and shortening the preparation cycle [81]. Xie et al. [82] used 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF₄) ionic liquid (IL) as a soft template in combination with KOH activation to synthesize 3D porous carbons (ISPCs) from coal tar (Figure 7(a)). The fabricated 3D ISPCs have a high SSA (1593 m²/g) and an abundance of pores, providing active sites and transport channels for ion adsorption. 3D interconnected frameworks avoid restacking of carbon sheets and can accelerate charge transfer. Due to these synergistic structural properties, the SCs assembled by ISPCs have high S_c (314 F/g at 0.05 A/g), good multiplicative performance (195 F/g at 100 A/g), and excellent cycling stability (97.1% capacitance retention after 10,000 cycles at 5 A/g) in KOH electrolytes. Li et al. [83] synthesized a series of N-doped porous carbon materials by sol-gel method using pentane-1,5-bis(dimethyl hexadecyl ammonium bromide) as a soft template, 3-aminophenol-formaldehyde resin as a carbon source and tetraethyl orthosilicate (TEOS) as a silicon source (Figure 7(b)). Carbon nanospheres with different morphologies were prepared using different doses of ethanol and surfactants. The synthesized N-doped mesoporous carbon spheres (NMHCSs) achieved a SSA of 1517 cm²/g, a

pore volume of 3.22 cm³/g, interconnected mesopores, and a high ratio of heteroatoms N and O doping. The S_c was 240 F/g at 0.2 A/g and 92% of the capacitance was still present at 10 A/g after 5000 cycles. At present, researchers have studied the synergistic effect of the soft template and hard template. Xi et al. [84] reported a soft/hard-template assisted method for the preparation of electrode materials. The phenolic resin was used as the carbon source, MgAl layered double hydroxide (MgAl-LDH) as the hard template, and triblock copolymer F127 as the soft template. MgAl-LDH drives the formation of vertically aligned mesoporous arrays in ordered mesoporous carbon sheets (OMCSs), which enhances the electrochemical performance in SCs (Figure 7(c)). Using polyvinyl alcohol (PVA)/H₂SO₄ gel as the electrolyte, symmetric SCs were prepared with a S_c of about 208 F/g and an E_d of up to 28.9 Wh/kg.

3.2.3. Self-templates

With the development of nanomaterial synthesis technology, in addition to the above-mentioned template method, porous carbon materials can also be prepared without the help of templates in recent years. Template-free methods mostly use organic molecules and inorganic

clusters as nano-construction units to assemble porous materials with suitable pore structures [85]. A common class of porous materials created with the present template-free technique is metal-organic frameworks (MOFs) [86]. They are composites with coordination network structures composed of organic ligands and metal cores. By carbonization in an inert atmosphere, the organic ligands retain the carbon skeleton while the metal cores are transformed into metal or metal oxide particles, which are eventually removed by dilute acid cleaning and leave the mesoporous structure [87,88]. It was mainly due to the optimal reconstruction of the pore structure of carbon due to the etching effect of acid. Compared with classical carbon structures, MOFs-derived carbon inherits the structural advantages of their precursor, and can achieve heteroatomic doping of carbon materials due to the presence of organic ligands. Jayaramulu et al. [89] prepared high surface area layered carbon nanosheets (NPS) with controlled porosity by the pyrolysis of metal-organic frameworks (MOF). By adding active redox substance (KI) to the conventional H_2SO_4 electrolyte, the NPS-800 electrode provided an S_c of $21.4 \mu\text{F}/\text{cm}^2$, and the assembled SCs had a high E_d of $90 \text{ Wh}/\text{kg}$. Deng et al. [90] prepared hierarchically porous honeycomb carbon frameworks (HHCFs) by pyrolysis and activation of metal-organic framework composites. The HHCF electrodes provide a high S_c of $361 \text{ F}/\text{g}$ at a C_d of $1 \text{ A}/\text{g}$ and a retention rate of 50% at $100 \text{ A}/\text{g}$ in an aqueous electrolyte. In addition, the symmetrical SCs fabricated in 1-ethyl-3-methylimidazolium tetrafluoroborate electrolyte exhibited a high S_c of $174 \text{ F}/\text{g}$ and provided an E_d of $74 \text{ Wh}/\text{kg}$ at a P_d of $872 \text{ W}/\text{kg}$.

3.3. Heteroatom doping

Due to their adaptable physicochemical characteristics, potential electrode material options include heteroatom-doped carbon compounds with a variety of surface functional groups [31,91,92]. The heteroatoms such as oxygen (O), nitrogen (N), phosphorous (P), sulfur (S), boron (B), and fluorine (F) can come directly from the precursors or be introduced by post-treatment (Figure 8) [9]. A fundamental role of heteroatom doping is to impart an additional pseudocapacitance to the carbon material through the Faraday reaction [93]. The content and type of heteroatom-containing reagents determine the physical and chemical properties of the material, controlling the morphology of the material and thus improving its electrochemical properties [94]. According to the number of doped heteroatoms, heteroatom doping is divided into single-component and multi-component styles.

3.3.1. Single-component heteroatom-doped carbon

Nitrogen is the most studied heteroatom for modifying carbon materials [95]. N is in group VA in the periodic table. The radius of the N atom is close to that of the C atom, and the physical and chemical properties are similar, so the distortion of the porous carbon lattice after the incorporation of the N atom is slight. After the N atoms carry lone pair electrons into the carbon skeleton, they can act as carriers in order to boost the charge density of the carbon material and achieve a significant improvement in the electrical conductivity of the porous carbon material [96]. In addition, N-doping can also increase the defect sites of carbon materials and introduce a variety of nitrogen-containing groups, hence enhancing the surface chemical activity of carbon materials and improving the application performance of materials in energy storage, heterogeneous catalysis, and chemical adsorption [97]. N-doping mainly exists in carbon materials in three ways: pyridine nitrogen, pyrrole nitrogen and graphite nitrogen. Pyrrole nitrogen and pyridine nitrogen substitute C atoms at the edge or internal defects of graphene to form one N and two C atoms linked sp^2 hybrid structures, which are six-membered rings and five-membered rings, respectively. Graphite nitrogen is a nitrogenous species with three sp^3 hybridized and three-dimensional structures formed by one N and three C atoms. There are two types of regularly used synthesis pathways for nitrogen-doped carbon materials, one method is to dope the N atoms directly into the formed carbon skeleton by pyrolysis or chemical vapor deposition (CVD), such as PANI, PPy, melamine, cyanamide, polyacrylonitrile, and other polymers [98–101]. Another approach is to post-treat carbon precursors with reactive N sources, such as urea, HNO_3 , or especially NH_3 [102–104]. And the post-treatment can further increase the amount of nitrogen doped into the feedstock, but this doping method is generally only possible at the edges of the material. Yang et al. [105] prepared N-doped porous carbon nanofiber aerogels (N-PCNFA) by a one-pot method. Using melamine as a nitrogen source, PAN/ZIF-8-based porous carbon nanofibers and graphene sheets were constructed as a three-dimensional framework (Figure 9(a)). The obtained materials have large SSAs and abundant pore structures, and N atoms are also merged into the carbon materials as active sites for Faradaic redox reactions. Therefore, the N-PCNFA electrode exhibits excellent performance with a high S_c of $279 \text{ F}/\text{g}$ at $0.5 \text{ A}/\text{g}$, with pseudocapacitance contributing about 46%. N-doped porous carbons were prepared by mixing potassium citrate and urea by Sevilla et al. [106] (Figure 9(b)). The SSA is $3350 \text{ m}^2/\text{g}$, the pore volume is $2.65 \text{ cm}^3\text{g}^{-1}$, and the nitrogen content is in the range of $0.5 \sim 4.5 \text{ wt } \%$. The assembled SCs exhibit a

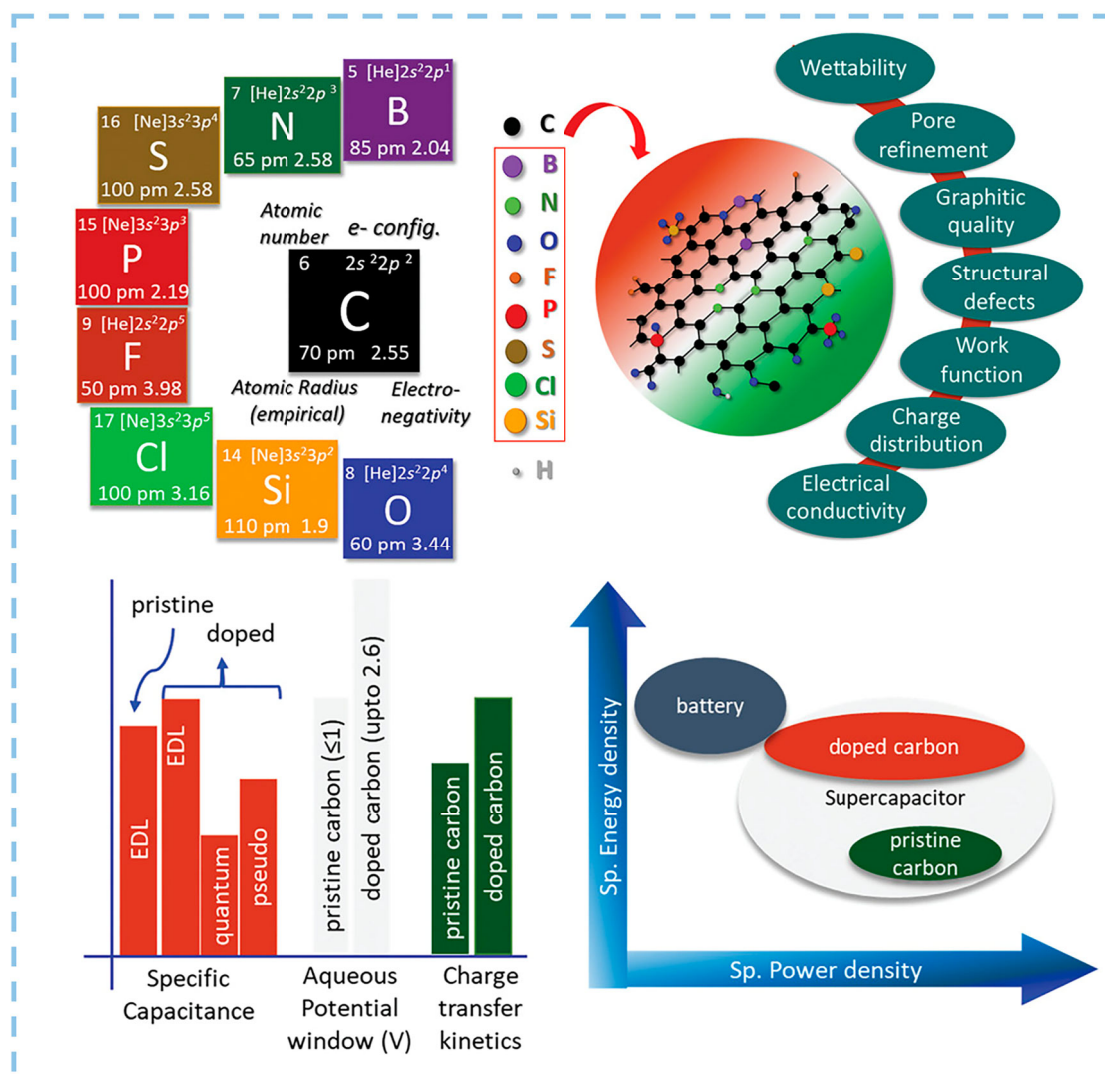


Figure 8. Schematic of carbon doping and its influences on the physicochemical properties for energy storage applications [9]. Copyright 2020, Wiley-VCH.

S_c of 44 F/g and an E_d of up to 56 Wh/kg in ionic liquid electrolyte.

Functional groups with an O atom are divided into basic functional groups (such as carbonyl ketones and quinones) and acidic functional groups (such as $-\text{OH}$, $-\text{COOH}$, $-\text{COO}$, and $\text{C}_6\text{H}_5\text{OH}$) [107]. In general, these groups work better in acidic and basic aqueous electrolytes compared to neutral aqueous electrolytes [108]. In addition, O can improve the wettability of the hydrophobic carbon surface to aqueous electrolytes. The S_c of carbon materials with different O-containing functional groups increases by $\sim 30\%$ in aqueous electrolytes. However, too many O-functional groups can reduce the conductivity of the material, hindering the entry of ions into the pores. Therefore, controlling the quantity of these groups is crucial for pseudocapacitive applications [108]. O-doped is generally rarely present in the form

of individual doping but exists in the form of co-doping with N, S, and P atoms.

The atomic radius of B is slightly smaller than that of C, and B doping can maintain the original sp^2 hybrid and conjugated planar structure of carbon materials, accelerate the transfer speed between charges and adjacent carbon atoms, and then improve the electrochemical performance of the material [109]. When B is doped into the carbon skeleton, its low electronegativity can considerably increase the ability to adsorb OH^- , which enhances its performance in aqueous electrolytes [110]. At present, when preparing B-doped porous carbon materials, commonly used B sources mainly include B_2O_3 , $(\text{NH}_4)_2\text{B}_4\text{O}_7$, H_3BO_3 , and $\text{BF}_3\text{-MeOH}$, etc. B atoms doped into the carbon skeleton exist mainly in the bonded forms of $-\text{BC}_2\text{O}$, $-\text{BCO}_2$, and $-\text{BC}_3$, among which $-\text{BC}_2\text{O}/-\text{BC}_3$ contains B-C bonds that greatly

N-doped

B-doped

P-doped

S-doped

Multi-doped

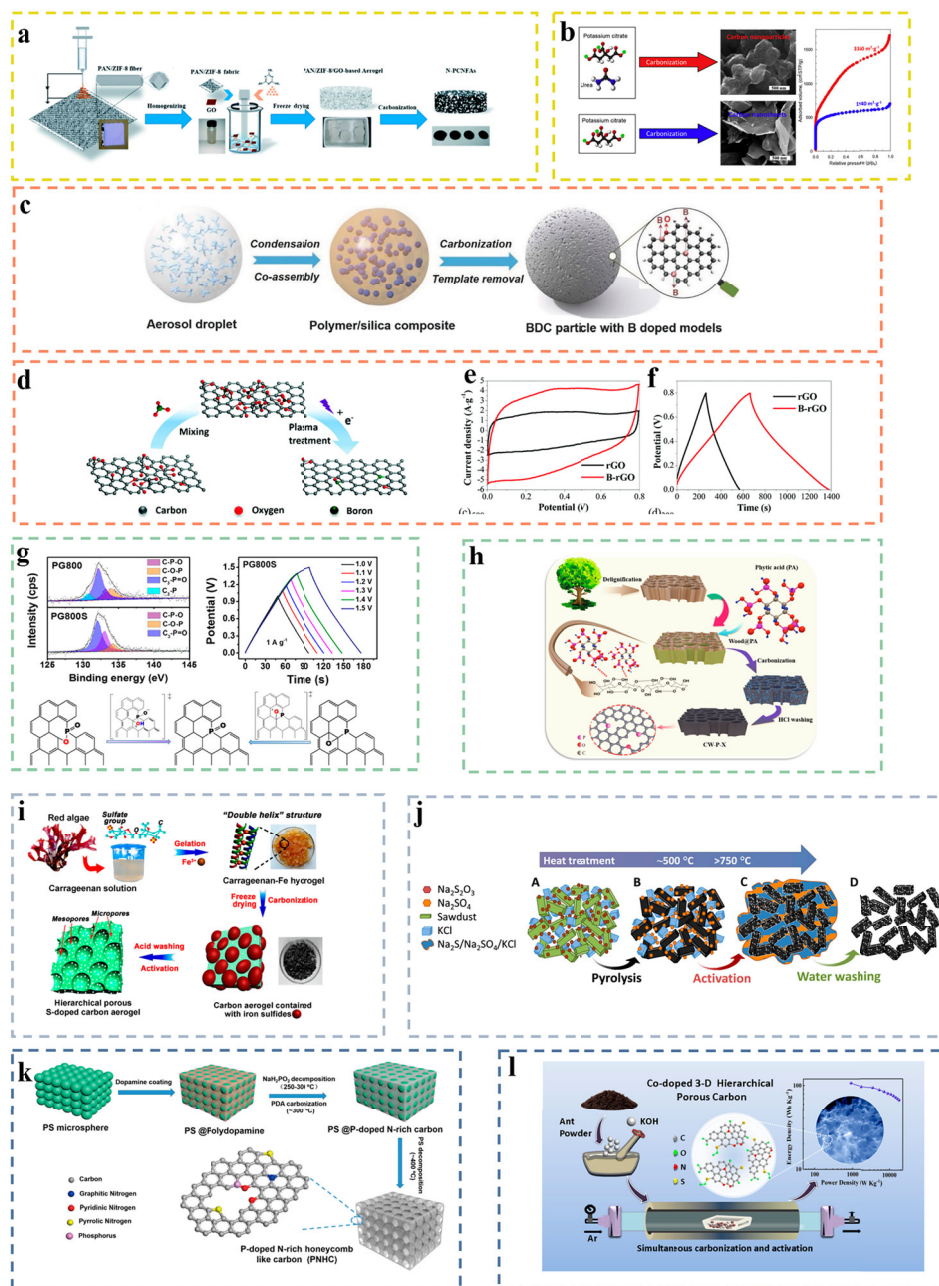


Figure 9. (a) Schematic illustration of the synthetic steps of N-PCNFAs [105]. Copyright 2020, The Royal society of chemistry. (b) Illustration of the synthesis and characteristics of the porous carbon obtained using potassium citrate and a potassium citrate/urea mixture [106]. Copyright 2018, Elsevier. (c) Schematic illustration of the BDC preparation process [112]. Copyright 2018, Wiley-VCH. (d) Schematic of the synthetic procedures of B-rGO. (e) CV curves of rGO and B-rGO. (f) Galvanostatic charge/discharge curves [113]. Copyright 2016, The Royal society of chemistry. (g) High-resolution P2p spectra and possible evolution mechanisms of phosphorus-containing compounds from intermediate transition states to defect C–P–O bonds galvanostatic, charge/discharge curves of each sample at 1 A/g at different potential windows in two-electrode symmetric SCs [116]. Copyright 2019, American Chemical Society. (h) Fabrication of the electrodes [118]. Copyright 2021, Elsevier. (i) The synthesis process of HPSCA [120]. Copyright 2019, Elsevier. (j) Illustration of the synthesis procedure [121]. Copyright 2019, Elsevier. (k) Fabrication process for PNHC [128]. Copyright 2019, Elsevier. (l) Schematic illustration of the production processes for the 3D hierarchical porous carbons [130]. Copyright 2018, Elsevier.

increase the stability of the carbon skeleton and improve the oxidation resistance of carbon materials [111]. The B–O–C structure contained in BCO_2 improves the surface wettability of the material. Sun et al. [112] reported a B-doped carbon realized by a continuous spray-assisted

co-assembly process. Using glucose and boronic acid as comonomers, the formation of B-containing carbon precursors through dehydration condensation between hydroxyl groups enables the in-situ and uniform doping of B atoms into the carbon framework (Figure 9(c)).

Boron doping leads to the grafting of additional oxygen to the carbon surface, which enhances the wettability and durability of the fabricated carbon electrodes. The constructed symmetric aqueous SCs achieve an E_d of 9.1 Wh/kg at a P_d of 24.1 kW/kg. Li et al. [113] prepared high-performance B-doped reduced graphene oxide (B-rGO) (Figure 9(d)). The material has a high S_c of 446 F/g at 0.5 A/g, which surpasses that of graphene oxide that has not been doped. In addition, the multiplicative performance of B-rGO is also outstanding (Figure 9(e,f)).

Compared to carbon, P has a weaker electronegativity and a larger volume, showing positive charge characteristics. The introduction of P in carbon materials can efficiently change the electronic structure and improve the performance of pseudocapacitors [92,114,115]. P-doped can increase the oxygen content of the material by forming C–P–O, C_3 –P, C–O–P, C_3 –P=O, and other groups [116]. Among them, C_3 –P=O can improve the stability and surface wettability of the material in the electrolyte, and reduce the impedance of ion transport, thereby effectively broadening the ESW of the carbon material in the aqueous electrolyte and obtaining better capacitance performance [117]. The phosphorus-doped graphene oxide prepared by Bi et al. was obtained by H_3PO_4 activation and high-temperature passivation (Figure 9(g)) [116]. Optimization of the phosphorus-containing functional groups is accompanied by a more uniform content and distribution. In order to maintain and modify the structure and surface chemistry of carbon materials, phosphorus is mostly present in carbon materials as C_3 –P=O and in very tiny amounts as metastable C–P–O. These properties enable P-doped graphene-based electrodes to exhibit an ESW of 1.5 V in aqueous electrolytes. Wang et al. [118] reported an electrode with a P content of up to 9.24 at% (Figure 9(h)). The electrode material used porous wood as the carbon source and phytic acid as the activator. The six negatively charged phosphoric acid groups of phytic acid provided the active sites for P-doping. The assembled SCs exhibited a high S_c of 4.7 F/cm² and 206.5 F/g at a C_d of 1.0 mA/cm².

As a heteroatom with similar electronegativity to C, S often exists in the edge region or defect site of the C-plane in the form of thiophene, sulfone group, thioether, sulfur oxide, etc. These sulfur-containing groups can adjust the electronic structure of carbon precursors, and they usually take the form of surface functional groups of carbon materials. Among them, the sulfone group and sulfur oxide can also increase the pseudocapacitance of carbon materials through redox reaction with the assistance of thiophene sulfur [119,120]. Unlike N, B, and P atoms, S and C are very close in electronegativity. Hence, the charge density of carbon materials is not significantly affected by S doping, and is more on producing a certain

spin density on the graphene surface [119]. Li et al. [120] prepared a three-dimensional hierarchical S-doped carbon aerogel (HPSCA) (Figure 9(i)). The material uses carrageenan-Fe hydrogel as a precursor, where Fe^{3+} acts as a pore-forming agent and carrageenan provide the conductive carbon skeleton. The abundant sulfate group in carrageenan can easily introduce S heteroatoms into the carbon lattice by pyrolysis. HPSCA has a macro-, meso-, and microporous coexistence structure and a SSA of 4037 m²/g with an S-doping content of about 0.83 at%. It has a S_c of 335 and 217 F/g at 1 A/g in aqueous and organic electrolytes, respectively. Sevilla et al. [121] prepared an S-doped (2 ~ 6 wt%) high SSA porous carbon with wood sawdust and tannic acid as carbon sources, sodium thiosulfate as the activator, and potassium chloride as a confining medium for the activation reaction (Figure 9(j)). The obtained porous carbon has a SSA of up to 2600 m²/g and a pore volume of 2.3 cm³/g, and as an electrode material the S_c up to 200 F/g.

3.3.2. Multi-component heteroatom-doped carbon

Compared to single heteroatom doped, multi-component heteroatom doped can improve the total electrochemical properties of the material because of the synergistic impact of multiple atoms [122,123]. After introducing the heteroatom, the p-orbital hybridization between the heteroatoms and C atoms leads to the redistribution of the electrons in the p orbital, thus regulating the electronic structure of the carbon itself or the surrounding carbon. In contrast to negatively charged N-6 and N-5, which can operate as Faraday reaction sites and cause pseudocapacitance, positively charged quaternary ammonium salts are thought to enhance electron transport in the carbon lattice [124,125]. The addition of N, B, F, S, and P doping not only boosts the wettability of the electrode surface and raises pseudocapacitance, but also enhances the characteristics of carbon materials by altering the electrical conductivity of nearby C atoms [126]. Lu et al. [127] prepared N/S double-doped carbon materials by a hypercrosslinking polymerization method, and N/S-containing precursors introduced heteroatoms into the carbon and changed the electron cloud density of the peripheral carbons, thereby realizing additional pseudocapacitance. The symmetric capacitor assembled with this electrode material provides a S_c of 464 F/g at 0.2 A/g and high E_d of 16.2 Wh/kg at P_d of 50 W/kg. He et al. [128] prepared N/P double-doped honeycomb 3D porous carbon materials using polystyrene microspheres as templates, trimethylolmethyamine and sodium hypophosphite as N and P sources, respectively (Figure 9(k)). The N/P double-doped enhances the pyridine nitrogen content and conductivity of the material and the surface-active sites. The material exhibited high

Table 1. A summary of electrochemical properties of heteroatom-doped materials in carbon-based SCs.

Electrode material	Electrolyte	Heteroatom content	Capacitance (F/g)	The energy density (Wh/kg)	Ref.
N-doped multi-chamber carbon microspheres	6 M KOH	N: 4.58 wt%, O: 2.12 wt%	301	–	[131]
N-doped porous carbon nanofibrous microspheres	EMIMTFSI	N: 2.4 at%, O: 6.1 at%	113	58.7	[132]
N/P co-doped 2D porous carbon nanosheets	2M KOH	N: 3.47 at%, P: 2.64 at%	322.9	17.04	[133]
O/N-co-doped porous carbons	6 M KOH	O: 18.76 at%, N: 1.70 at%	270	14.8	[134]
N/S-doped porous carbon	6 M KOH	N: 4.5 at%, S: 5.8 at%	464	16.2	[127]
N/O-doped hierarchical porous carbon nanorods	EMIMBF ₄	N: 8.1 wt%, O: 10.0 wt%	214	116.5	[135]
N/S-co-doped carbon nanobowls	6 M KOH	N: 3.3 wt%, S: 1.7 wt%	279	9.6	[136]
Honeycomb-like porous carbon foam	1 M Na ₂ SO ₄	N: 1.1 at%, O: 11.2 at%	260	29.3	[137]
B/N-co-doped carbon nanosheets	1 M Na ₂ SO ₄	N: 3.1 at%, B: 0.5 at%	235.6	30.1	[138]
N/S co-doped hierarchical porous carbon nanorods	6 M KOH	N: 5.8 at%, S: 0.44at%	282	39.15	[139]
O, N, and P codoped hierarchical porous carbon	6 M KOH	O: 8.61 at%, N: 7.95 at%, P: 1.34at%	230	7.5	[140]
O, N, S-tridoped carbon	6 M KOH	O: 9.94 at%, N: 1.60at%, S: 1.31at%	409	11.3	[141]

reversible S_c of 419.3 mA h/g at 100 mA/g, and high multiplicity performance (10 A/g, 119.5 mA h/g) when used for potassium ion batteries. Wang et al. [129] used nitrogen and phosphorus-rich phosphonitrilic chloride trimer ($\text{Cl}_6\text{N}_3\text{P}_3$) to fabricate N, P, and O triple-doped carbon (NPOC), which showed a wide ESW (1.25 V) in the KOH electrolyte, showing that it is the multiple doping of N, P and O that promotes the storage of more cations on the surface of the doped carbon electrode. These adsorbed cations can effectively suppress the hydrogen precipitation reaction during charging, which leads to a wider voltage window. Zhao et al. [130] reported the O–N–S co-doped carbon (HPC) from ant powder, and the resulting product had a large SSA (2650 m²/g), a typical 3D framework, and interconnected hierarchical porous structures (Figure 9(l)). An ultra-high S_c of 576 F/g was achieved in KOH electrolyte. The symmetrical SCs fabricated using the EMIMBF₄ electrolyte provide an E_d of up to 107 Wh/kg at a P_d of 900 W/kg. The electrochemical properties of more heteroatom-doped materials are listed in Table 1.

3.4. Carbon composites

In the field of composite materials, the ideal materials are those that not only don't have the flaws of their separate parts, but also gain from the synergistic benefits that the parts have when combined [142]. Composites are usually composited with carbon materials using pseudoactive species metal oxides and conducting polymers,

the former being modified based on electron transfer mechanisms to complement pseudocapacitance [22,143]. Also, using carbon as a carrier for the preparation of composites can improve the electrochemical utilization of pseudoactive sites and also serve as an effective conductive pathway to improve electron transfer and mechanical stability [144].

3.4.1. Carbon/metal-oxide composites

In the domains of electrochemical SCs and hybrid devices, several metal oxides, including V₂O₅, Fe₃O₄, Co₃O₄, NiO, RuO₂, MnO₂, and TiO₂, have undergone substantial research. Metal oxides can provide pseudocapacitance, carbon substrates act as conductive carriers and provide double-layer capacitance. The clever combination of the two is expected to achieve the effect of 1 + 1 greater than 2. The layered hybrid composite of CuCo₂S₄/carbon nanotubes (CNT) prepared by Li et al. [145] The CNT embedded in the CuCo₂S₄ matrix provides many efficient pathways for electron transfer and ion diffusion, thus facilitating the Faraday reaction of the CuCo₂S₄ electrode during energy storage. The assembled asymmetric SCs (ASC) have an E_d of 23.2 Wh/kg at a P_d of 402.7 W/kg. Asim et al. [146] prepared fused nanostructures of branched RuO₂ nanorods (NR) developed directly on carbon nanotube-modified carbon cloth (CNTS-CC). The synergistic effect of metal oxide NR and highly interconnected CNT-CC provides a larger surface area and exposed active sites, thus allowing easier access of ions/electrolytes to the electrode (Figure

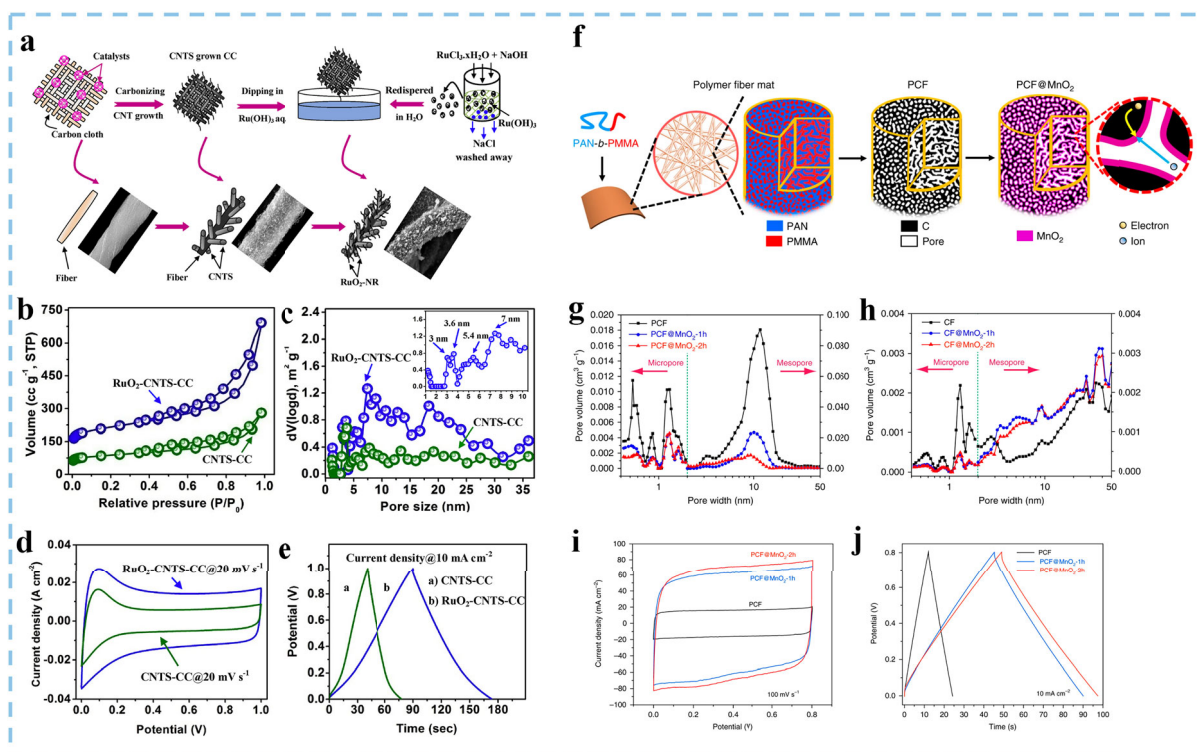


Figure 10. (a) Schematic illustration of RuO₂-CNTS-CC preparation. (b) Nitrogen sorption/desorption isotherms. (c) Pore size distribution using DFT methods. Electrochemical performance of different electrodes in liquid state SCs using 1 M H₂SO₄ electrolytes: (d) Comparison of CV at 20 mV s⁻¹. (e) GCD curves at 10 mA cm⁻² [146]. Copyright 2019, Elsevier. (f) Schematic illustration of the synthesis of PCF and PCF@MnO₂. (g, h) Pore size distributions. (i) CVs at a scan rate of 100 mV s⁻¹. (j) Galvanostatic charge-discharge curves at 10 mA cm⁻² [148]. Copyright 2019, Springer Nature and the authors.

10(a)). From the adsorption isotherms (Figure 10(b,c)), RuO₂-CNTS-CC has a larger SSA and a higher plateau of the hysteresis loop, confirming the superior hierarchical porosity. Compared with CNTS-CC, the CV curve area of the RuO₂-CNTS-CC electrode is increased, indicating the main contribution of RuO₂ NRs to the significantly improved charge storage. The S_c of RuO₂-CNTS-CC is as high as 1760 mF/cm², which is twice that of CNTS-CC (Figure 10(d,e)).

Due to their inexpensive cost and low toxicity compared to other transition-metal oxides, MnO₂-based electrodes for energy storage applications are gaining popularity. Liu et al. [147] prepared a SCs electrode with MnO₂ and N-doped hollow carbon spheres (NHCS) composite. The MnO₂ nanosheets were grown on the surface of NHCS through the redox reaction between NHCS and potassium permanganate (KMnO₄) in an aqueous solution. The NHCS increases the electrical conductivity of the composites and facilitates the acceleration of electron transfer during charging and discharging to enhance cycling stability. The MnO₂ layered structure provides abundant active sites. The hollow internal structure shortens the electrolyte diffusion path and provides sufficient ions for the high-speed Faraday reaction. The

S_c of MnO₂-NHCS composites is 392 F/g at 0.5 A/g, which is 1.6 times higher than that of MnO₂ HSs. Liu et al. [148] filled a porous carbon fiber (PCF) with MnO₂ less than 2 nm thick. Mesopores and manganese dioxide with a thickness of 2 nm allow fast electron/ion transport within the electrode material (Figure 10(f)). Two carbon fibers were synthesized, namely poly (acrylonitrile-block-methyl methacrylate) (PAN-b-PMMA) derived PCF with uniform mesopores, and one made from pure polyacrylonitrile (PAN) with limited mesoporous carbon fiber (CF). Uniform mesopores are crucial to achieving high-quality loading of MnO₂ on CF. A large number of mesopores provides a large available SSA for loading MnO₂ on PCFs, while the micropores play a limited role (Figure 10(g,h)). PCFs with uniform mesopores exhibit excellent rapid charge transport and large mass loading. The S_c of MnO₂ reaches 1148 F/g. (Figure 10(i,j)).

3.4.2. Carbon/conductive polymer composites

Conductive polymers, a class of organic polymers that conduct electricity through conjugated π -bonds in polymer chains [149], are typical Faraday electrode materials and widely used in SCs, such as polyaniline (PANI) [150], polypyrrole (PPy) [151], and polythiophene (PTh) [152].

However, although conductive polymers generally have higher S_c than pure carbon materials, their electrochemical performance is not outstanding when assembled into practical devices. In addition, the ionic intercalation and deintercalation of conductive polymers during the Faradaic reaction can cause volume expansion and contraction, resulting in short electrode cycle life. As a result, mixing conductive polymers with carbon materials is expected to overcome the above shortcomings, so as to achieve the coexistence of high S_c and cyclic stability.

Zhang et al. [153] created a three-dimensional interconnected porous carbon (PC/PANI) hybrid by growing PANI in situ on nanosheets heated with potassium citrate. The macropores/mesopores of the PC provide approachable active sites, allowing the uniform distribution of stacked vertically PANI on the PC. Due to the synergistic effect of three-dimensional PC and PANI, the composite exhibits an excellent S_c of 512 F/g at a C_d of 1 A/g. Furthermore, the assembled asymmetric SCs have a high E_d of 22.3 Wh/kg at a P_d of 700 W/kg. Zhuo et al. [151] reported layered porous carbon aerogels. Cellulose was the carbon precursor and also the support for the conducting polymer polypyrrole (PPy). Micro-, meso-, and macropores coexist in the 3D porous carbon aerogel/PPy composites that have been created, allowing for quick electrolyte transfer and effective PPy penetration into the carbon network. The combination of layered porous carbon aerogel and conductive polymer produced a S_c of 387.6 F/g at 0.5 A/g, with 92.6% capacitance retention after 10000 cycles.

4. Electrolytes

Electrolytes are essential ingredients of SCs, providing charged ions involved in charge storage. Their characteristics have a significant impact on the overall performance of the SCs. To develop carbon-based SCs with high E_d , electrolytes need to exhibit a wide ESW and fast ion diffusion [13,154]. Electrolytes are a major factor limiting the operating voltage of SCs. The electrolytes commonly used in SCs are aqueous solutions, ionic liquids and organic substances. The two main criteria for electrolyte selection are ESW and ionic conductivity. A stable and wide electrochemical window plays an important part in the E_d of the SCs, while the ionic conductivity has an equally important effect on the P_d of the device.

Generally speaking, the requirements for a perfect electrolyte are as follows: (1) a significant ESW, (2) a broad operating temperature range, (3) high ionic conductivity, (4) excellent compatibility with electrolyte materials, (5) high electrochemical stability, (6) sensitivity to the environment, (7) high chemical inertness, (8) low volatility, and (9) low cost. Each electrolyte has

unique superiority and limitations, making it challenging for one electrolyte to satisfy all of these criteria. It has prompted many study into enhancing the functionality of electrolytes in general [13].

4.1. Aqueous electrolytes

4.1.1. Traditional aqueous electrolytes

Aqueous electrolytes have been used extensively in research and development due to their easy handling in the laboratory compared to organic electrolytes and ILs, which require purification procedures [155]. The aqueous electrolyte exhibit high conductivity, which is advantageous for reducing the equivalent series resistance and improving the power delivery of SCs [156]. In addition, the charge storage capacity, cost and security of aqueous supercapacitors are also better than those of non-aqueous supercapacitors. However, the low operating voltage due to the decomposition of water at 1.23 V leads to poor energy density (≤ 10 Wh kg^{-1}), which seriously affects the commercial application of aqueous SCs. Therefore, it is very attractive to develop an aqueous electrolyte with a large working voltage.

The pH, which is closely related to the O_2 and H_2 evolution potentials of the aqueous systems, should be taken into consideration while choosing the electrode materials [157]. Aqueous electrolytes fall into three categories: alkaline, acidic, and neutral solutions. As mentioned earlier, the main drawback of aqueous electrolytes is their relatively narrow ESW, limited by water decomposition. For instance, when oxygen evolution takes place at a positive electrode potential of approximately 1.23 V and hydrogen evolution takes place at a negative electrode potential of approximately 0 V vs. SHE, the resulting SCs have a cell voltage of around 1.23 V [158]. Safety and efficiency would be compromised as a result of the gas evolution, which could also lead to ruptures of SCs cells. The cell voltage for SCs with aqueous electrolytes is typically limited to ~ 1.0 V to prevent gas evolution.

The practical operating voltage windows of acidic and alkaline electrolytes tend to be lower than those of neutral electrolytes, most likely due to their higher concentrations of H^+ and OH^- ions, resulting in a lower excess potential [159]. Alkaline electrolytes are among the most widely used aqueous electrolytes in literature applications. Alkaline and acidic electrolytes also exhibit strong ionic conductivity, which is favorable for high-power performance. As an example, compared to non-aqueous electrolytes, the ionic conductivities of 6 M KOH and 1 M H_2SO_4 electrolytes are almost 600 and 800 mS cm^{-1} , respectively. The neutral electrolyte has a large voltage window and less corrosion. Generally, the working voltage of neutral water electrolytes is $1.0 \sim$

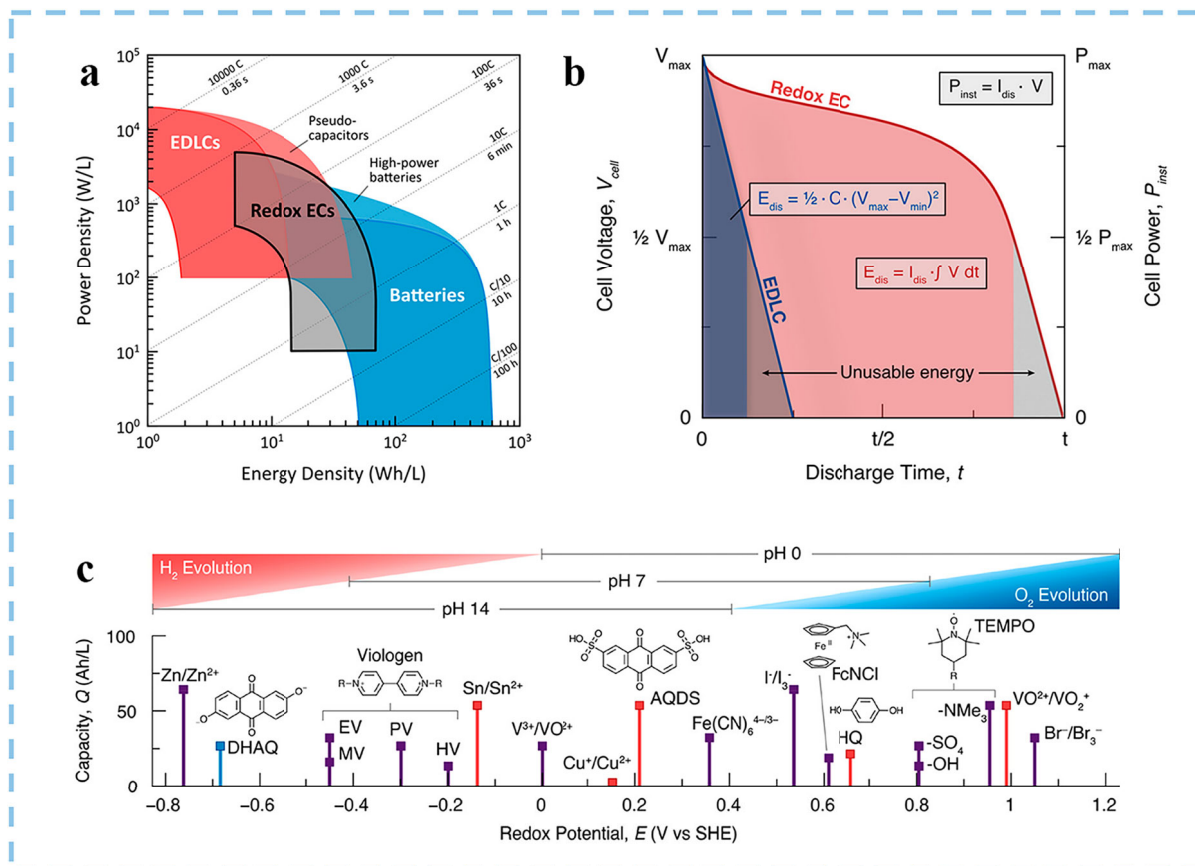


Figure 11. (a) Ragone plot illustrating the range of device-level power and energy density for EDLCs, pseudocapacitors, secondary batteries, and redox EDLCs. (b) Discharge profiles of an ideal EDLC and a redox EDLC. (c) Reduction potential and demonstrated volumetric capacity for selected aqueous redox couples used in redox EDLCs, flow batteries, and redox batteries [160]. Copyright 2017, American Chemical Society.

1.4 V, and the S_c of SCs with this electrolyte are usually lower than those with acidic and basic electrolytes. However, more studies have shown that neutral electrolytes inhibit hydrogen evolution (HER) and oxygen evolution reaction (OER) through low H^+ and OH^- concentrations, so neutral electrolytes show higher working voltage (> 1.5 V) than alkaline and acidic electrolytes (≤ 1.0 V). Various neutral electrolytes have been used in electric double-layer capacitors and hybrid capacitors, such as alkali metal chloride (NaCl, etc.), sulfate (Na_2SO_4 , etc.), nitrate ($LiNO_3$, etc.) and acetate ($NaCH_3COO$, etc.).

4.1.2. Adding redox-active mediators (RMs)

In recent years, adding dissolved redox-active RMs to the aqueous electrolyte provides additional Faradaic contribution to the surface redox reaction based on the original energy storage, which becomes a very effective means to improve its E_d . In addition, the introduction of redox-active RMs can effectively improve the ionic conductivity, thus increasing the specific capacitance. The advantages of this method are as follows [160]: (1) easy to dissolve, (2) no requirement for electrode materials, (4) structure

can be customized, (3) high power performance. Redox electric double-layer capacitors (redox EDLCs) are very encouraging energy storage devices between conventional EDLCs and batteries (Figure 11(a)). Under constant current discharge conditions, the energy transferred is proportional to the area under the time-voltage curve. As seen in Figure 11(b), the redox EDLC has higher E_d and more stable power output [160]. The earliest redox electrolytes discovered include alkali metal iodide salts and hetero-poly acids. Hydroquinone (HQ) and methylene blue in sulfuric acid [161]. Other series of redox-active molecules including organic molecules (viologens, quinones), halides, inorganic and organometallic complexes (metal bipyridyl complexes, ferricyanides), and transition metals (Cu, V, Fe) were studied [162–164]. Figure 11(c) provides an overview of the reported redox-active electrolytes and their accompanying redox potentials. The addition of the active redox electrolyte only partially replaces the original inert electrolyte that cannot contribute to the capacity, so the mass of the added redox active electrolyte can be ignored in the calculation [160].

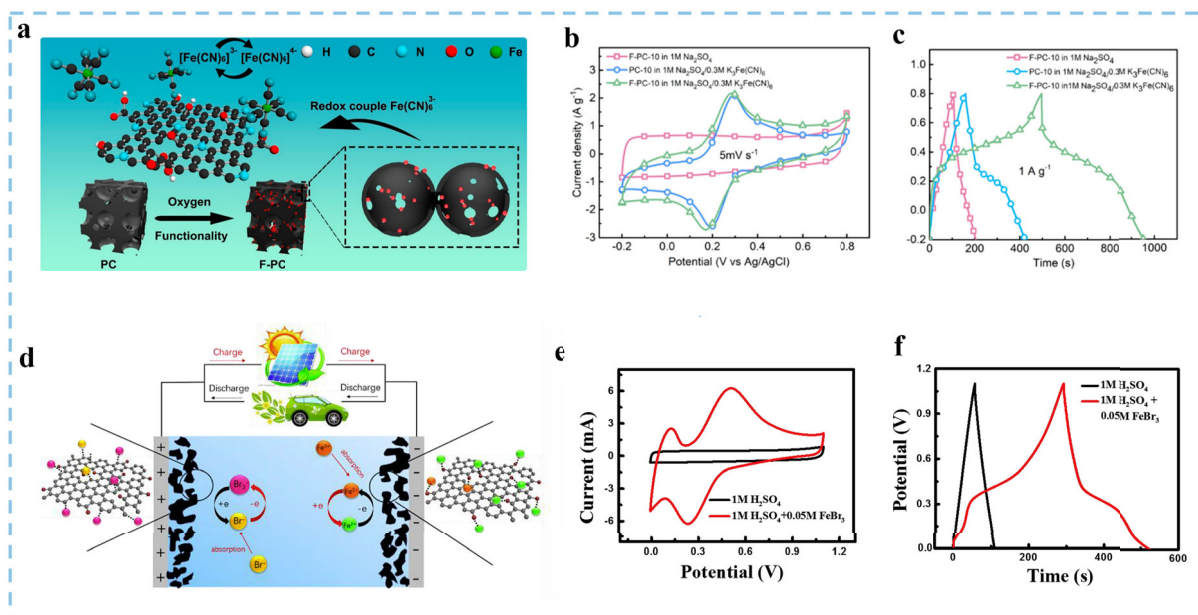


Figure 12. (a) Synthesis Route of F-PC and the Illustration of the Effect on Oxygen Functional Groups and Interconnected Pore Structure during Energy Storage. (b) CV curves at 5 mV s^{-1} . (c) GCD curves at 1 A g^{-1} [165]. Copyright 2018, American Chemical Society. (d) Schematic of the energy storage in redox EDLC using the electric double-layer for capacitive charge storage and redox-active electrolyte in the electrolyte for faradaic charge storage. (e) CV curves at a scan rate of 5 mV s^{-1} . (f) Galvanostatic charge/discharge curves at a C_d of 2 A g^{-1} [169]. Copyright 2019, Elsevier.

Yan et al. [165] used a synthetic porous carbon (F-PC-10) in combination with the nature of redox electrolytes to adsorb Fe(CN)_6^{3-} ions in a mixed electrolyte of $1 \text{ M Na}_2\text{SO}_4/0.03 \text{ M K}_3\text{Fe(CN)}_6$ for the redox reaction. Figure 12(a) is a schematic diagram of the energy storage mechanism. During the charging process, electrons are transferred from the positive terminal to the negative terminal via an external circuit, resulting in a potential difference between the positive and negative electrodes. F-PC-10 acts as a negative electrode to adsorb cations (K^+ and Na^+) in the surrounding electrolyte. The anions SO_4^{2-} , Fe(CN)_6^{3-} , and Fe(CN)_6^{4-} move to the positive electrode, and the $\text{Fe(CN)}_6^{3-}/\text{Fe(CN)}_6^{4-}$ redox reaction occurs on the surface of the positive electrode, resulting in additional Faradaic contribution, thus achieve higher E_d . The CV curves of F-PC and PC are shown in Figure 12(b). The pattern of adding $\text{K}_3\text{Fe(CN)}_6$ electrolyte has obvious redox peaks. F-PC has a high S_c of 454 F/g at 1 A/g (Figure 12(c)), and can retain 88% of the capacity after 10000 cycles. The assembled SCs introduced $\text{Fe(CN)}_6^{3-}/\text{Fe(CN)}_6^{4-}$ at an operating voltage window of 1.8 V , allowing the F-PC-10-based EDLC to present an E_d of 36.9 Wh/kg at a P_d of 225 W/kg . Currently, it has been reported that dual redox electrolytes employing anolyte/catholyte can match the capacitance of redox-enhanced electrodes, fully fulfilling the promise of redox electrolytes [166–168]. Wang et al. [169] used an $\text{H}_2\text{SO}_4/\text{Na}_2\text{SO}_4$ electrolyte with FeBr_3 as a dual redox additive and did not differentiate between the cathode

and anode electrolytes in EDLC (Figure 12(d)). During the charging process, the cations H^+ , Na^+ , Fe^{2+} , and Fe^{3+} move toward the negative electrode and generate additional Faraday redox reactions $\text{Fe}^{2+}/\text{Fe}^{3+}$. The anions Br^{3-} , Br^- , and SO_4^{2-} move toward the positive electrode and generate additional Faraday redox reactions $\text{Br}^{3-}/\text{Br}^-$ on the positive electrode surface. When 0.05 M FeBr_3 was added to $1 \text{ M H}_2\text{SO}_4$, S_c reached 885 F/g , more than four times that of $1 \text{ M H}_2\text{SO}_4$, and had good stability after 10,000 cycles (Figure 12(e,f)). In $0.5 \text{ M Na}_2\text{SO}_4 + 0.05 \text{ M FeBr}_3$, E_d reached 40 Wh/kg .

4.1.3. Water-in-salt (WIS) electrolytes

For traditional aqueous electrolytes, the best development direction is to choose a salt solution with appropriate ion concentration, which is mainly due to the fact that the ionic conductivity usually decreases with the high concentration of electrolyte. Therefore, the development of WIS electrolytes has become a hotspot in the study of aqueous electrolytes. Fascinatingly, as neutral electrolyte increase, the operating voltage window of these electrolytes can be clearly shown to have enlarged. It was found that ultra-concentrated water-in-salt electrolytes (WIS) with very high salt-to-water molar ratios can significantly reduce the activity of water, thereby enlarging the ESW. A WIS electrolyte is defined as an aqueous solution in which the mass and volume of the salt are greater than the mass and volume of the solvent. SCs using WIS electrolytes not only have a wide voltage

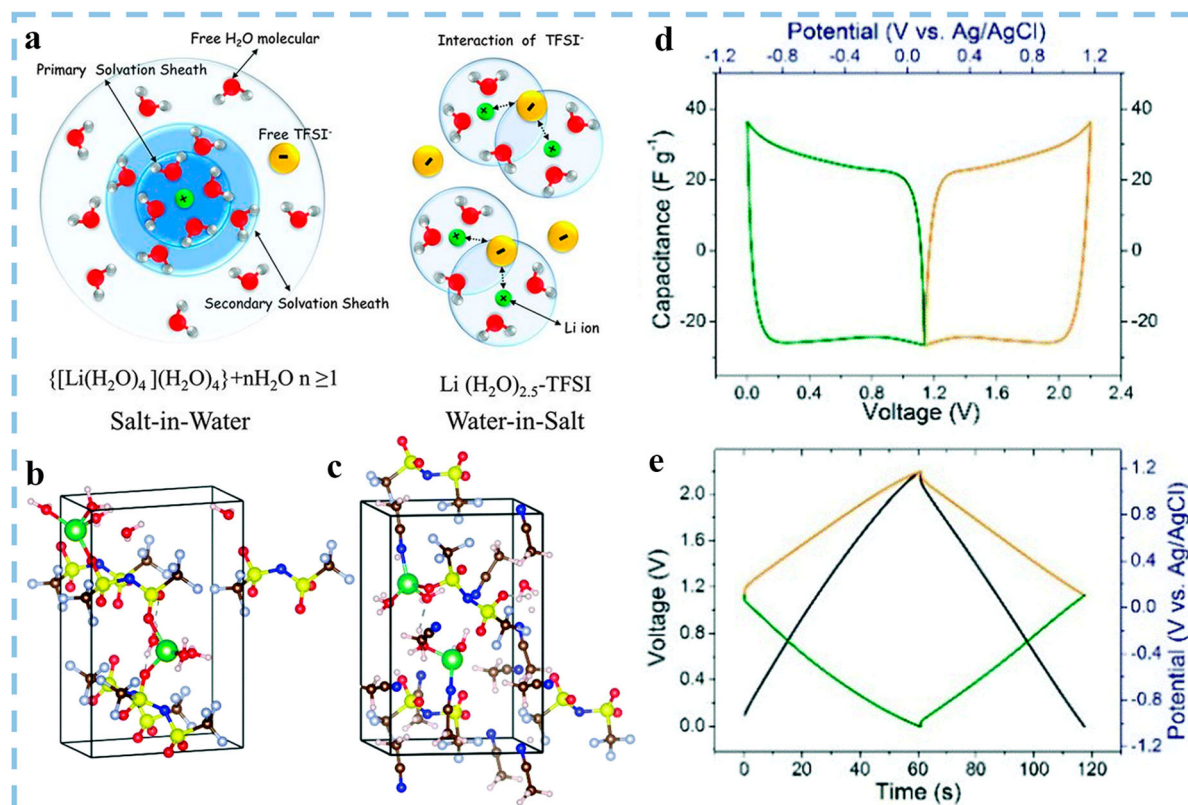


Figure 13. (a) Illustration of the evolution of the Li primary solvation sheath in diluted and water-in-salt solutions [159]. Copyright 2020, Wiley-VCH. (b) Snapshots of the 21 M WIS electrolyte and (c) the 5 M AWIS electrolyte during DFT-MD simulations. Atom colors: Li, green; O, red; H, pink; C, brown; N, blue; S, yellow; and F, gray. (d) CV curves at a scan rate of 50 mV/s. (e) GCD curves at a C_d of 1 A/g of the full cell (black curves), the positive electrode (orange curves), and the negative electrode (olive curves) [176]. Copyright 2018, The Royal society of chemistry.

window but also maintain the advantages of high Pd and safety in an aqueous system [170]. Suo et al. [171] first reported an electrolyte by dissolving lithium bis (trifluoromethanesulfonyl) imide (LiTFSI) in extremely high concentrations (> 20 M) in water, showing a wide ESW of 3 V. LiTFSI is a lithium salt with high solubility in water, which is stable and not easily hydrolyzed. Water-in-salt means that the mass and volume of the solute salt are higher than the mass and volume of the solvent. Interestingly, the LiTFSI hyper-concentrated electrolyte with a solubility of 21 M presents a stable potential window of 3 V, which is because the HER and OER starting overpotential of this electrolyte exceed its thermodynamic potential. On the one hand, the hyper-concentrated aqueous electrolyte presents a different solvated shell structure because the average number of water molecules for ion dissolution is much less in the super-concentrated aqueous electrolyte than in the dilute electrolyte (salt-in-water). The high concentration leads to a solvated shell layer of lithium ions containing anions with lithium ions and water molecules creating strong coordination between them, thus reducing the electrochemical activity of water. On the other hand, the crystal-like structure

of the super-concentrated aqueous electrolyte allows for a higher reduction potential of TFSI⁻ than the isolated TFSI⁻ and hydrogen precipitation potential. As the result, the anode/electrolyte contact formed a substantial layer of LiF as a result of the TFSI⁻ reduction. The formation of the LiF layer further inhibited the reaction between TFSI⁻ and water (Figure 13(a)). In combination with anodic passivation and inhibition of HER and OER, the ESW of this ‘salt-in-water’ electrolyte is increased to 3 V [159]. A high concentration (~ 28 M) electrolyte containing 7 M LiOTF and 21 M LiTFSI was obtained by Suo et al. [172] through the introduction of a second salt. It can effectively form a protective interfacial phase on the anode while further suppressing the water activity on the anode and cathode surfaces. It exhibits a wider ESW of 3.1 V.

These fairly stable ultra-concentrated WIS electrolytes have been frequently used in high-potential window aqueous Li-ion and Na-ion batteries [173–175]. However, the high viscosity and strong electrostatic attraction of WIS electrolytes limit the rate performance when used with SCs. Dou et al. [176] reported a co-solvent introduced into the salt solution by mixing acetonitrile with

21 M LiTFSI WIS electrolyte, a co-solvent was introduced into the salt solution to create an 'acetonitrile/brine water' (AWIS) electrolyte. A 5 M AWIS electrolyte was chosen as the optimum concentration, which is non-flammable and maintains a wide ESW of approximately 2.2 V at the stainless-steel electrode. As shown in Figure 13(b), in the 21 M WIS electrolyte, Li^+ is easily organized by the O atoms of water molecules, and the unsaturated Li^+ solvation sheath also allows TFSI $^-$ to partially coordinate with Li^+ , leading to strong ionic interactions. When acetonitrile was added to the 21 M WIS electrolyte (Figure 13(c)), the water molecule interacts strongly with Li^+ and inhibits the water activity. Acetonitrile molecules coordinate with lithium ions to form spaces for the Li^+ solvation sheath. Figure 13(d,e) shows the CV and GCD curves of the full cell and a single electrode at an ESW of 2.2 V. The positive and negative electrodes have almost symmetrical characteristics, indicating that the capacitive contributions of Li^+ and TFSI $^-$ are almost identical.

4.2. Ionic liquids

Ionic liquids (ILs) provide a technology of SCs composed of a large number of asymmetric organic cations and organic/inorganic anions. Compared with common solvents, ionic liquid usually presents complex and changeable structures under the synergistic action of hydrogen bond, electrostatic force and van der Waals force, so it gradually becomes one of the best alternatives for traditional organic electrolyte. Because of unique combination of physicochemical and electrochemical characteristics, ILs show a remarkable E_d and great safety [177]. Nevertheless, the high viscosity as well as low ionic conductivity of ILs severely restrict the quick growth of IL-based SCs [178–180]. ILs often possess several benefits, such as excellent thermic, chemic, inflammability (contingent on the connection of cations and anions), minimal volatility, and electrochemical stability [181]. Due to the wide multifariousness of cation and anion concoctions found in ILs, their physical and chemical characteristics may also be finely tuned [182]. ILs are also thought of as 'designer solvents' in this sense [13]. The electrolytes of ILs can achieve operating voltages significantly higher than 3 V. The electrolyte compositions may be modified or tailored to satisfy specific criteria of energy storage performance [179,180,183]. This attribute tenability of ILs is particularly favorable for SCs electrolytes. The applied ILs for an energy storage device in the published literature are frequently on the basis of phosphonium cations, imidazolium, ammonium, sulfonium, pyrrolidinium, and so on. Typical anions of ILs are dicyanamide (DCA $^-$), bis(trifluoromethanesulfonyl)imide (TFSI $^-$), bis(fluorosulfonyl)imide (FSI $^-$), hexafluorophosphate (PF $_6^-$), and tetrafluoroborate (BF $_4^-$) [184–186].

ILs can generally be divided into protic, aprotic, and polymeric kinds according to their composition [187]. The working voltage (1.2 ~ 2.5 V) of EDLCs with protic ILs is significantly lower than that of EDLCs with aprotic ILs [188,189]. However, compared with aprotic ILs, protic ILs have generally been cheaper and synthesized more simpler [188]. Aprotic ionic liquids have weaker interactions between anions and cations, which improves their ionicity and electrochemical stability relative to protic ionic liquids [190–192]. EMIMBF $_4$ is one of the most widely studied ionic liquids. ILs have extremely strict requirements on the pore size distribution of electrode materials. Many researchers began to use carbon materials with different pore size distributions to match ILs. Li et al. [193] reported a large microporous carbon with a major void size of 1–2 nm, where the contribution of the large microporous volume to the total microporous volume reached 70.1% (Figure 14(a)). The assembled symmetric SCs were operated at 3 V in EMIMBF $_4$ electrolyte, and the CV diagram showed a perfect rectangular shape with a S_c of approximately 48.9 F/g at a C_d of 0.5 A/g (Figure 14(b,c)). Chen et al. [194] studied ionic liquid (EMIMBF $_4$) electrolytes for nitrogen-sulfur co-doped graphene aerogel (NS-GA) electrode composites (Figure 14(d–f)). The symmetric SCs have an ESW of 3.8 V in EMIMBF $_4$ ILs, a S_c of 203.2 F/g at 1 A/g of C_d , and capacitance retention of 90% over 3000 cycles. With E_d up to 100.7 Wh/kg at a P_d of 0.94 kW/kg, the electrochemical properties of the bombardment depend mainly on the layered porous structure of, for example, the synthetic material.

4.3. Organic electrolytes

Due to the limited factors such as low operating-voltage window in aqueous electrolyte, commercial supercapacitors focus on the research of organic electrolytes. Organic electrolyte consists of conductive salt and organic solvent. The cations of conductive salts are generally provided by quaternary ammonium and lithium salt, and the anions are mainly PF $_6^-$, ClO $_4^-$ and BF $_4^-$. Organic solvents are propylene carbonate (PC), acetonitrile (ACN) and ethyl methyl carbonate (EMC), etc. Customarily, the organic electrolyte used for SC comprises an organic solvent and a conductive salt dissolved in it [13]. Conductive salts provide adsorbed ions for the SCs energy storage process, commonly known as tetraethylammonium tetrafluoroborate (TEABF $_4$) and triethylmethylammonium tetrafluoroborate (TEMABF $_4$). Organic solvents mainly provide a working environment for ion transport processes, and commonly used ones include acetonitrile (ACN),

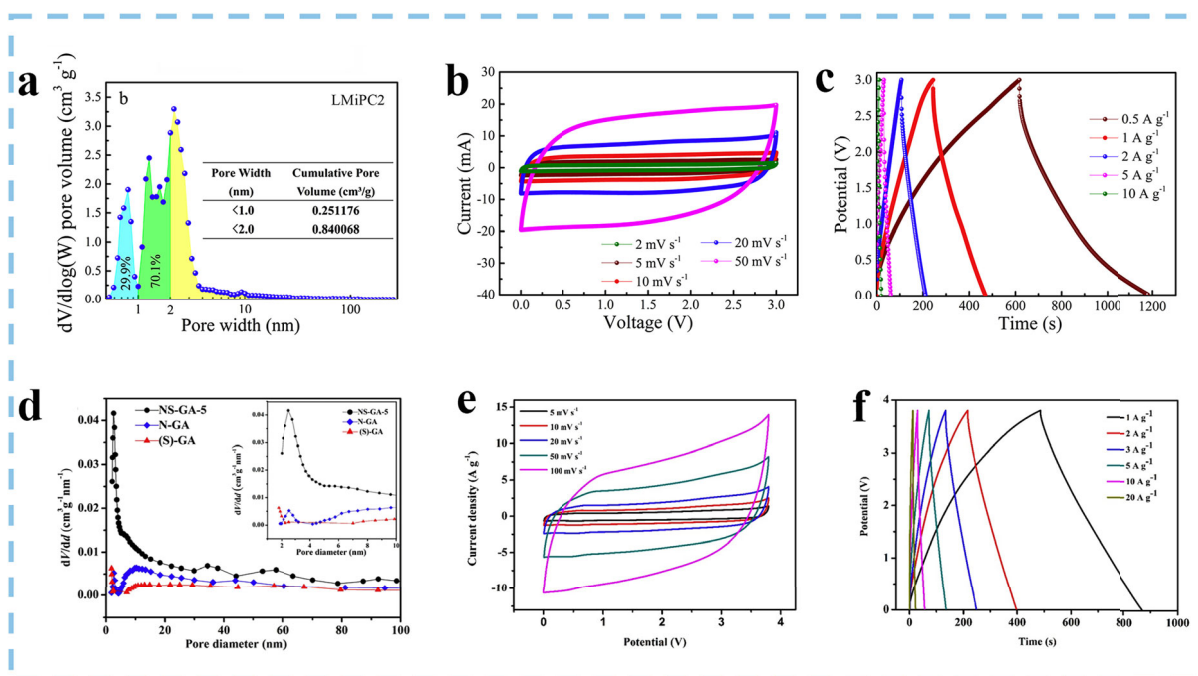


Figure 14. (a) Pore size distribution of the sample. (b) CV curves of the SCs device in EMIMBF₄ at various scan rates. (c) GCD curves at various current densities [193]. Copyright 2020, Elsevier. (d) Pore size distribution calculated from the adsorption isotherms using BJH method, and the inset is the amplification at small pore diameter. (e) CV curves at different scan rates. (f) GCD curves at various current densities [194]. Copyright 2018, Elsevier.

propylene carbonate (PC), gamma-butyrolactone (GBL), and N, N-dimethylformamide (DMF). The commercial industry is now dominated by devices based on organic electrolytes owing to their elevated voltage window (2.5 ~ 3.0 V) [195]. The low corrosiveness of the organic electrolyte allows the use of collectors and encapsulating shells made of inexpensive metals such as aluminum. Nevertheless, organic electrolytes are burdened by dissatisfied ionic conductivity ($10 \sim 50 \text{ mS cm}^{-1}$), ignitability, volatility, and toxicity in comparison with aqueous electrolytes [196,197]. The S_c of an EDLC is shown to be dependent on both the pore size dispersion of the carbon materials and its particular surface area [198]. The pores of working electrodes are directly connected to the features of organic electrolytes, such as the dimensions of anion and cation species and ion-solvent interaction [199]. Koh et al. [200] reported on the impact of the ionic size of diminutive quaternary ammonium BF₄ salts on electrochemical double-layer capacitors. Using microporous activated carbon electrodes, around 10% higher capacitance was attained with TMEA BF₄ and TMPA BF₄ relative to TEA BF₄, in defiance of the C_d . In addition, these salts are as stable as TEA BF₄ in cyclic life measurements (Figure 15(a,b)). Ions in narrow pores throw off their solvated shells as they access deeper and narrower rooms. Smaller desolvated ions move more readily within the narrow pores, increasing capacitance at

whole currents. Although small pores in carbon composite can improve the SSA, they can also restrict the ability of the bigger organic ions to pass through the electrodes and reduce the S_c . It is essential to improve S_c by matching the size of the electrolyte ions to the size of the pores in the carbon material [201]. It was demonstrated that in the presence of holes that were almost the same size as the desolvated ions, the S_c of EDLCs might abnormally increase. Sun et al. [202] successfully synthesized 3D vertically aligned graphene nanosheet arrays (3D VAGNAs) using biomass waste from spruce bark, which has a 3D interconnected structure, an ultra-high SSA of about $2385 \text{ m}^2/\text{g}$, an average pore volume of about $1.68 \text{ cm}^3/\text{g}$, and effortlessly attainable exposed surfaces of graphene nanosheets (Figure 15(c)). The high available surface area can adsorb ions, thus leading to superior S_c . The open pores of the nanosheets can act as ion buffer reservoirs to shorten diffusion distances and accelerate electron transfer, and the 3D graphene structure enhances conductivity and electrochemical stability. Benefiting from the multitudinous synergistic effects of these advantages, VAGNA presents an excellent electrochemical performance in organic electrolytes. With 1.0 M TEABF₄/AN as an electrolyte, the fabricated SCs have a high S_c of 239 F/g at a C_d of 1 A/g in an ESW of 3.0 V, and a high E_d of 74.7 Wh/kg at a P_d of 743.7 W/kg (Figure 15(d,e)). The importance of the pore size distribution

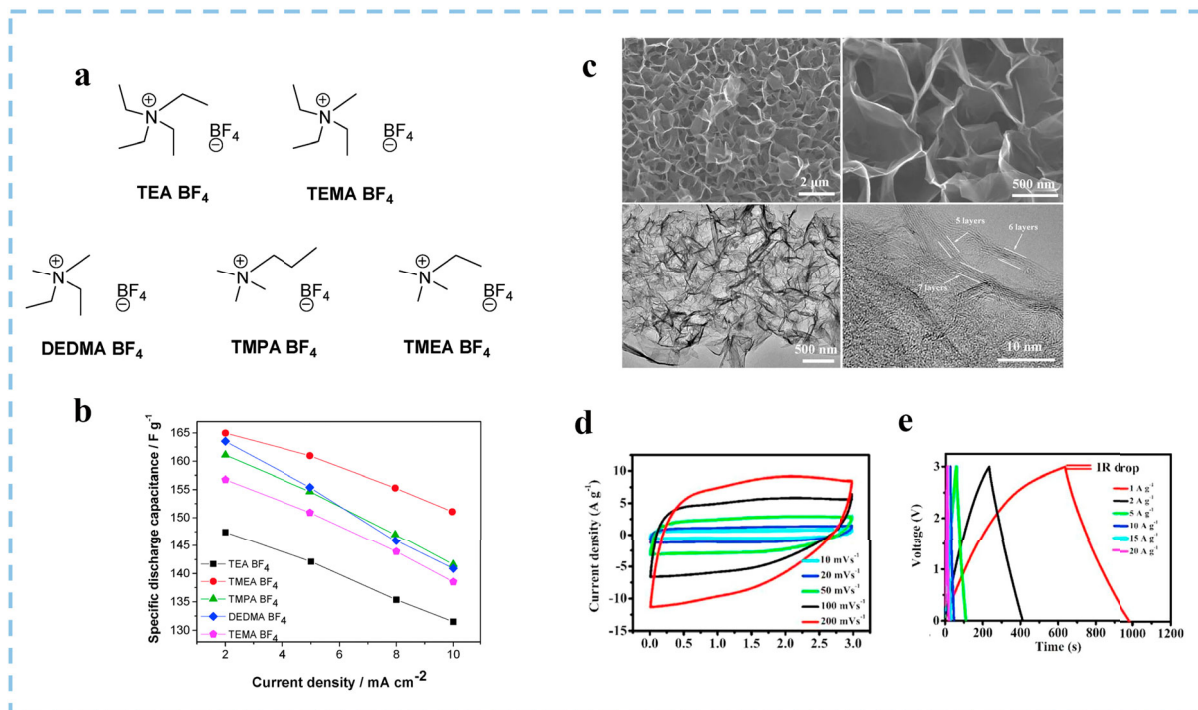


Figure 15. (a) Structures of quaternary ammonium BF_4 ions. (b) Capacitance values at low currents [200]. Copyright 2014, The Royal society of chemistry. (c) SEM and TEM image of VAGNA-900. (d) CV curves at various scan rates. (e) GCD curves at different current densities [202]. Copyright 2018, Elsevier.

Table 2. Electrochemical behavior of organic electrolytes in carbon-based SCs.

Electrode material	Electrolyte	Cell voltage (V)	Energy density (Wh/kg)	Specific Capacitance (F/g)	Ref.
Highly porous interconnected carbon nanosheets	1M TEABF ₄ /ACN	2.7	25	120–150	[203]
AC	0.7M TEABF ₄ /ADN	3.75	~28	25	[204]
Heteroatom-doped porous carbon flakes	1M LiPF ₆ / (EC-DEC 1:1)	3	29	126	[205]
AC	1.5M SBPF ₄ /PC	3.5	52	122	[206]
AC (MSP-20)/mesoporous Nb₂O₅-carbon	1M LiPF ₆ /EC-DMC (1:1)	3.5	74	—	[207]
mesophase carbon microbeads/ graphitized carbon commercial AC	1.5M TEMABF ₄ /PC	4	30	—	[199]
porous graphitic carbon//Li₄Ti₅O₁₂	1M LiPF ₆ /EC-DMC (1:1)	3	55	—	[208]
3D interconnected porous activated carbon	1M TEABF ₄ /AN	2	16.52	119	[209]
Nitrogen-doped nanoporous activated carbon	1 M TEABF ₄ /AN	3	42	133	[210]
porous carbon sheets	1 M TEABF ₄ /AN	2.7	38.2	221	[211]
Nitrogen-doped reduced graphene oxide electrodes	1 M TEABF ₄ /ACN	2.9	149.4	563	[212]
Highly mesoporous carbon flakes	1 M TEABF ₄ / PC	2.6	24	—	[213]
Few-layer graphene-like nanosheets	1 M Et ₄ NBF ₄ /EC-DCE	2.5	68	78.3	[214]

of carbon materials for capacitance enhancement. The SCs based on organic electrolytes and the corresponding properties are summarized in Table 2.

5. Summary and perspectives

Most carbon materials are highly conductive, environmentally friendly, and easy to design. All organic substances contain carbon, which is the basic and also the sixth most prevalent element in the crust of the Earth. The extraordinary reliability of carbon in various electrolyte solutions enables conductive carbon materials to

be used in various electrochemical systems and devices. Therefore, carbon can be deemed among the most important electrode materials in SCs. The key to attaining high E_d in carbon-based SCs is the improvement of S_c and ESW, which is advantageous for extending their range of practical applications. In this article, we summarize recent advances in the two core components of electrode materials and electrolytes in carbon-based SCs. Carbon-based electrode materials can be enhanced by increasing SSA, modulating the pore structure, doping with heteroatoms and carbon composites to increase S_c . In addition, the research progress of aqueous, organic,

and ionic liquid electrolytes is introduced to continuously seek ways to broaden the ESW. Although important progress has been made in recent years in the area of high E_d carbon-based SCs, it is recommended that future efforts continue to be made in the following areas:

- (1) Carbon-based SCs, as typical EDLCs, it is necessary to increase the S_c by introducing substances that can contribute to the pseudocapacitance. On the one hand, heteroatoms or metal oxides are introduced into the carbon material to increase the functional groups and active sites, and probably the presence of these substances does not contribute much to the pseudocapacitance of conventional electrolytes. It is expected to break through this bottleneck by exploring the internal relationship between the electrochemical behavior and the factors such as particle size, surface functional groups and heteroatom doping of carbon-based materials and their composites. On the other hand, the Faraday reaction is promoted by adding redox additives to the electrolyte. To investigate the energy storage mechanism of different functional groups and active sites interacting with redox additives to make the hidden pseudocapacitance in EDLCs fully functional.
- (2) In high E_d carbon-based SCs, it can be seen from the formula $E = 1/2CV^2$ that improving the ESW is more effective than the S_c . WIS and ionic liquid electrolytes have an overwhelming advantage in the study of high-voltage window electrolytes. This salt-solvent system has unlimited possibilities through salt and solvent mixing. By improving the ion dynamics and reducing the electrolyte viscosity, the overall E_d of carbon-based SCs is increased.
- (3) In carbon-based SCs, it is important to achieve a match between the carbon material and the electrolyte. Carbon materials are tuned by different mechanisms to obtain micro-, meso- and macroporous structures. Currently, the connection between precursor and electrode material structures is not clear. In the next work, how to obtain carbon-based electrodes for specific tasks needs to be further investigated. Also, molecular dynamics is used to study the energy storage mechanism in carbon structures to maximize electrode capacitance in specific electrolytes.
- (4) Carbon-based materials show great application potential in the direction of supercapacitors because of their environmental friendliness and simple preparation. In addition, their effective combination with carbon-based nanoparticles is expected to achieve all-carbon electrodes with high energy density and long cycle life. Advanced experimental

characterization combined with in-situ techniques can be used to reveal the influence mechanism of various possible factors on the performance of supercapacitors and the basic role in the electrochemical process, so as to guide the preparation and synthesis of high-efficiency electrode materials.

Carbon electrode/electrolyte compatibility can be optimized for the ideal device configuration. Micropore diameters are adjusted to accommodate electrolyte ions, and mesoporous/macropore pathways are introduced to transfer viscous media. Similarly, the choice of electrolytes can be changed according to the needs of the electrode material. Despite the great challenges in carbon electrode/electrolyte synergy, we believe that the high-energy, high-power, long-term operation of carbon-based SCs have good prospects for development.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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