Pitch-based carbon materials: a review of their structural design, preparation and applications in energy storage

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Abstract: Because of its high carbon content and easy graphitization, pitch is a promising precursor for carbon materials. To produce carbon materials with the desired performance, it is necessary to overcome the inherent shortcomings of pitch. For example, its complex composition and easy melting make it difficult to control the structure of the resulting carbon materials. Recently, researchers have proposed several methods to control the structure of carbon materials produced from pitch for energy storage applications. The latest advances in the structural design and preparation of pitch-based carbon materials for use in energy storage devices such as supercapacitors and alkali metal ion batteries are reviewed.

Key words: Pitch; Carbon materials; Preparation; Structural design; Energy storage

1 Introduction

This paper reviews the recent research progresses of pitch-based carbon materials as shown in Fig. 1. In order to obtain the carbon materials with controllable structure, various preparation methods are firstly introduced, such as solvent partition, template and pre-oxidation strategies. The material characteristics and structure regulation mechanism of these methods are also thoroughly analyzed. Then, the potential applications of pitch-based porous carbon in energy storage applications including supercapacitors (SCs) and alkali metal ion batteries are summarized. Finally, the remaining challenges and research prospects in the field are discussed.

With the large-scale consumption of fossil energy, it has become the research focus to save energy and develop renewable energy while realizing the rational and effective utilization of limited resources[1–2]. In the development and utilization of renewable energy, carbon materials play a crucial role because they can be widely used as electrode materials or important components in energy storage systems. In principle, carbon materials can be prepared from various carbon-containing sources. Generally, people tend to choose low-cost precursors such as biomass, polymers and pitch to produce various carbon materials.

China is rich in coal resources and the coking capacity ranks first in the world, the yield of coal tar pitch (CTP) from coking industry is about 50%-60%. Nowadays, the pitch is mainly used in traditional fields such as refractory, adhesive, anti-corrosion, waterproof and road building materials due to its good corrosion resistance and cohesiveness[3–6]. However, the above-mentioned traditional applications can only transform pitch into low added value products. Therefore, new applications are urgently needed to explore and develop to convert pitch into products with high value. Notably, pitch has merits of high carbon content, abundance and inexpensive price, which is considered as promising candidate to produce carbon materials. Currently, preparation of carbon material for energy storage has become an important route for deep utilization of asphalt because pitch is easy to be graphitized compared with biomass and synthetic polymer[7–9]. Up to date, a variety of carbon materials including carbon nanospheres, nanowires, nanosheets and networks have been prepared from pitch[10–12]. They have been widely evaluated to use as electrode material for supercapacitor (SCs), lithium ion, sodi-

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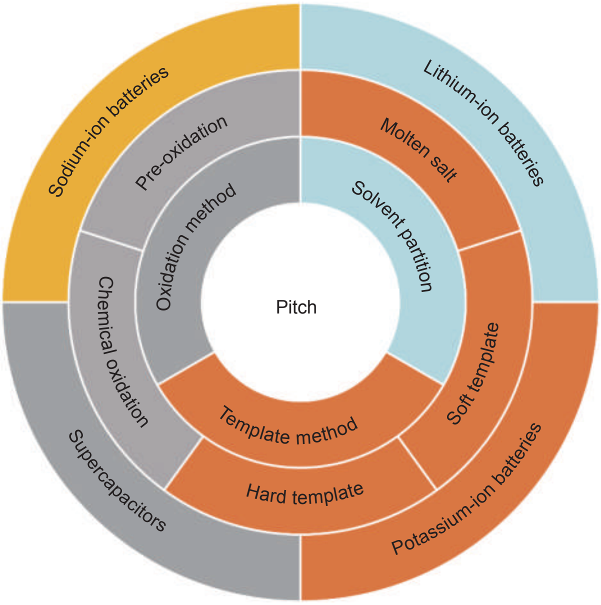

Fig. 1　Schematic illustration of synthesis strategy of pitch-based porous carbon and their applications in energy storage

um ion and potassium ion batteries[13–15].

Pitch can be divided into petroleum asphalt and coal tar asphalt due to different sources and processes of production. Generally, CTP contains polycyclic aromatic hydrocarbons, while the large polycyclic aromatic hydrocarbons are proved to be easily converted into the graphite structure[16–18]. However, the pitch possesses complex chemical compositions, which have a negative impact on regulating the structure and composition of the final carbon products. In the 1970s, researchers used organic solvents to segment the complex pitch components based on the principle of similar solubility into soluble substances in different solvents by using the organic solvents of quinoline, toluene, petroleum ether, n-hexanol, carbon disulfide and so on. Then, the substance with similar component and structure is subsequently studied[19–21]. The other feature for pitch is thermoplastic, that is, when the temperature reaches the softening point of pitch, the pitch will change from solid to liquid. Due to the existence of the above-mentioned characteristics, it is difficult to control the structure of the final carbon material during the conversion process of pitch. Therefore, templates such as magnesium oxide, calcium oxide, silicon dioxide and molten salts, are introduced into the system to regulate the pore structure and morphology of pitch-based carbon materials[22–24]. In addition to the template method, oxidation strategy has also been developed to prepare pitch-based porous carbon. During the process, functional groups will be introduced into the molecules of pitch to increase their reaction activity. Subsequently, the molecules react with each other to form macromolecules with similar structure to graphite, thus the structural stability of the intermediate product has been enhanced as the phase change is avoided during pyrolysis process[25–27]. Since that the morphology of carbon materials can be well controlled, the pitch-oxidation method has become an important strategy to prepare carbon materials.

Electrochemical energy storage performance of carbon materials is strongly depended on the pore structure, surface property and specific surface area. Pore engineering and heteroatom doping are effective strategies to improve the electrochemical performance of carbon materials[28–29]. For the pore engineering, it is essential to control the pore structures including pore volume, diameter and its distribution. Generally, there are micropores, mesopores and macropores exist in the carbon materials for energy storage. The micropores play a major role in the specific surface area of carbon materials and can provide rich active sites for electrolyte ion adsorption, whereas the micropores prevent rapid diffusion of electrolyte ions. Comparatively, mesopores can supply high-speed channels for ion transmission and diffusion. Macropores with larger size can be used as the storage tank of electrolyte ions to shorten the diffusion distance of electrolyte ions, whereas they make less contribution to the specific surface area of carbon materials[30–31]. Up to date, the hierarchical porous carbon materials with micropores, mesopores and macropores have been synthesized by the template, activation method, solvent partition and pre-oxidation methods. In addition to pore engineering, introduction of heteroatoms (e.g., oxygen, nitrogen, sulfur, phosphorus and boron, etc.) into carbon materials can not only improve the hydrophilicity to promote the charge transfer on the electrode/electrolyte interface, but also increase the pseudo-capacitance of carbon materials through reversible redox reactions[32].

2 Pre-treating process

2.1 Solvent partition method

CTP is a kind of mixture composed of polycyclic aromatic hydrocarbons and their derivatives[33–35]. The common solvent segmentation method is used to divide CTP into the components with similar structure and characteristics (e.g., volatility and softening point). The principle is that each component of pitch has different aromatization degree, composition and/or property, showing distinctive solubility in different organic solvents. Therefore, the selection of appropriate organic solvents allows for efficiently segmenting the pitch components. The widely-used organic solvents include quinoline, pyridine, tetrahydrofuran, cyclohexane, petroleum ether, gasoline, n-heptane, benzene and toluene[36–39]. After being segmented, the pitch sections have similar properties and become easy to control the structure of the obtained carbon materials. For example, Guan et al. have used toluene, quinoline and pyridine as extractants to divide CTP (softening point, 274 °C) into 2 parts: (1) light components of toluene and pyridine soluble substances, (2) heavy components of quinoline and quinoline insoluble substances (Fig. 2a). It is found that porous carbon materials are easily prepared from the light component by KOH activation, as it contains more volatile alkyl side chains. On the contrary, the

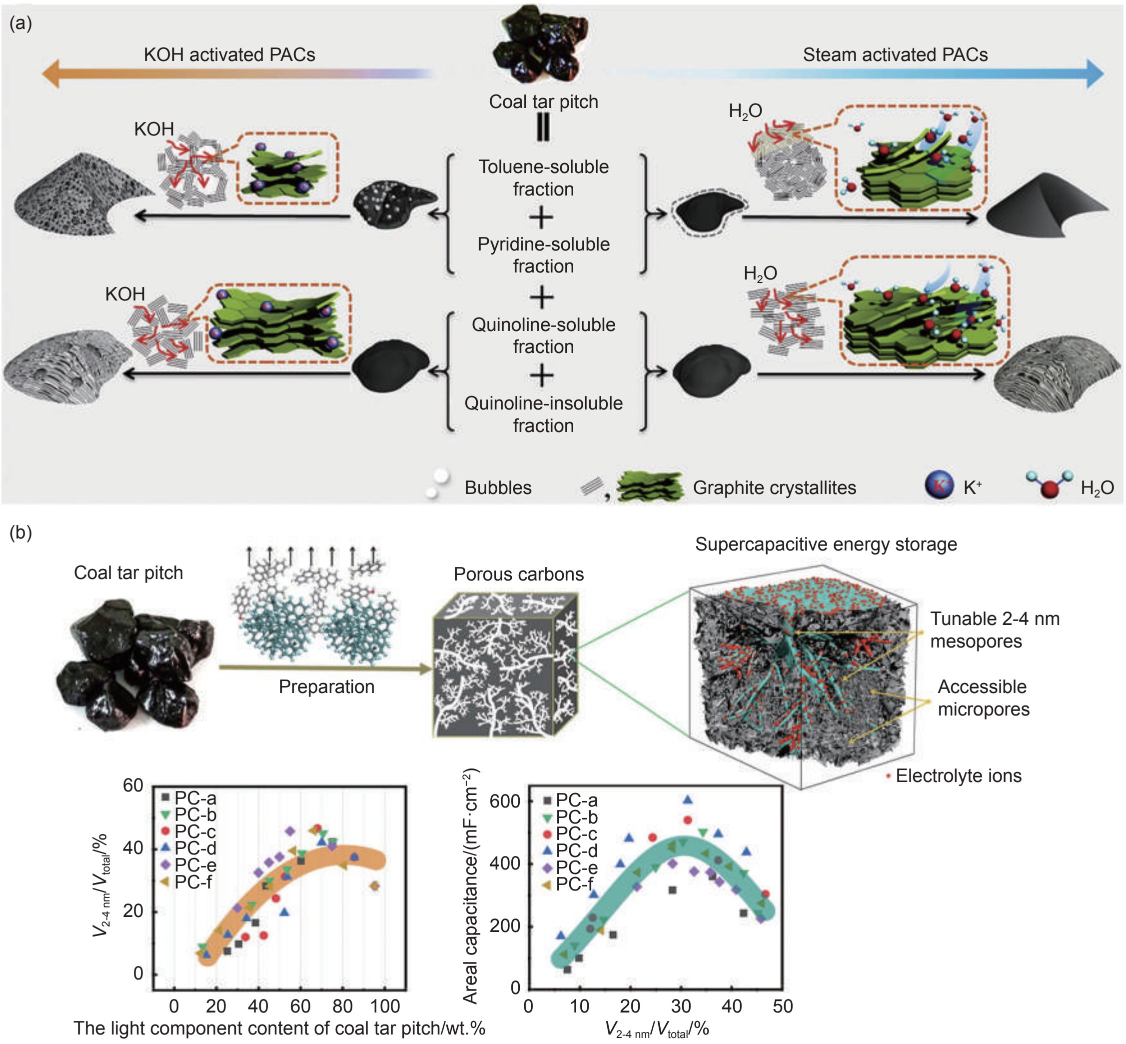

Fig. 2 (a) The illustration of the KOH-activated samples[40]. Copyright 2018 Elsevier Ltd. (b) The preparation process of PCs and the relationship between the TS content of MCTPs and the specific surface area, cumulative pore volume, and $V_{2\text{–}4\ nm}/V_{total}$ ratio of PCs[42]. Copyright 2020 Elsevier Ltd heavy component of CTP is easier to form rich pore structures under the activation of steam[40]. Further, immersing components (β-resin) (soluble in quinoline and insoluble in toluene) in concentrated sulfuric acid could obtain the sulfonated pitch molecules[41]. The oxygen containing functional groups such as sulfonic groups are introduced to the pitch molecules to increases the active sites, which can make pitch easier to crosslink.

Furthermore, as shown in Fig. 2b, the formation of small mesopores (2-5 nm) in porous carbon materials has been controlled by adjusting the content of light components in pitch molecules[42]. Additionally, Zhuang et al. divided the pitch into 6 components with carbon disulfide, acetone and ethyl acetate, and activated each component at high temperature[43]. The carbon materials obtained from different components show different electrochemical properties when they are used as electrode materials for SCs. It is found that the carbon material derived from the pitch component extracted from carbon disulfide demonstrates the best electrochemical performance. The above-mentioned results show that different components of pitch have an important influence on the pore structure and morphology of the carbon product.

2.2 Pre-oxidation method

Due to the conjugation of polycyclic aromatic hydrocarbons, the molecules of pitch tend to form stacked structure during the pyrolysis process, which is not conducive to form porous structure. Additionally, the rare functional groups in the molecules also greatly hinder the interaction with other compounds. Hence, the pitch needs to be modified before undergoing the process of synthesizing porous carbon[44–45]. Oxidation method can introduce oxygen containing functional groups into pitch molecules to improve the reactivity of pitch molecules. The cross-linking reaction between the functional groups makes the pitch molecules form a relatively stable structure, which is more conducive to the subsequent regulation of microstructure[46].

2.2.1 Chemical oxidation method

Strong oxidants such as hydrogen peroxide, nitric acid and potassium permanganate can introduce functional groups into the aromatic ring of pitch. The introduction of functional groups not only can improve the hydrophilicity of pitch, but also increase the active sites for energy storage[47–49]. Compared with hydrogen peroxide, stronger oxidant of nitric acid can not only introduce oxygen and nitrogen containing functional groups into the side chains of aromatic rings, but also break the side chains of aromatic rings in pitch molecules or the fat chains between aromatic rings, which weakens the conjugation effect between polycyclic aromatic hydrocarbons and reduces the excessive accumulation of pitch molecules[50]. Therefore, the pitch-based carbon materials obtained from the precursors oxidized by nitric acid had larger specific surface area and more pores than hydrogen peroxide (Fig. 3a-c). Yang et al.[51] have prepared 3D porous carbon from nitric acid oxidized pitch (Fig. 3d), in which the morphology of porous carbon was adjusted by adding ferric chloride and zinc chloride (Fig. 3e-h). The results show that the layered porous carbon is prepared under the condition of adding zinc chloride and ferric chloride at the same time due to the joint action of the activator of zinc chloride and the structure directing agent of ferric chloride. The strong oxidant of potassium permanganate has also been used to oxidize pitch. Zhuang et al.[52] have obtained the oxidized pitch by mixing pitch and potassium permanganate at room temperature and used this kind of pitch oxide as raw material to directly synthesize oxygen doped 3D porous carbon *via* salt template method. Summary, after introduction of functional groups into the PAHs side chain of pitch, the specific surface area and pore volume of the material can be controlled.

2.2.2 Pre-oxidation in air

Compared with the chemical oxidation method, air pre-oxidation method is more environmentally friendly because no strong oxidants are required. Pre-oxidation in air refers to introduce oxygen containing functional groups by heating pitch molecules at a relatively low temperature ($T < 400$ °C) in the air atmosphere[53]. Yang et al.[54] have used toluene soluble pitch as raw material to control the microstructure and

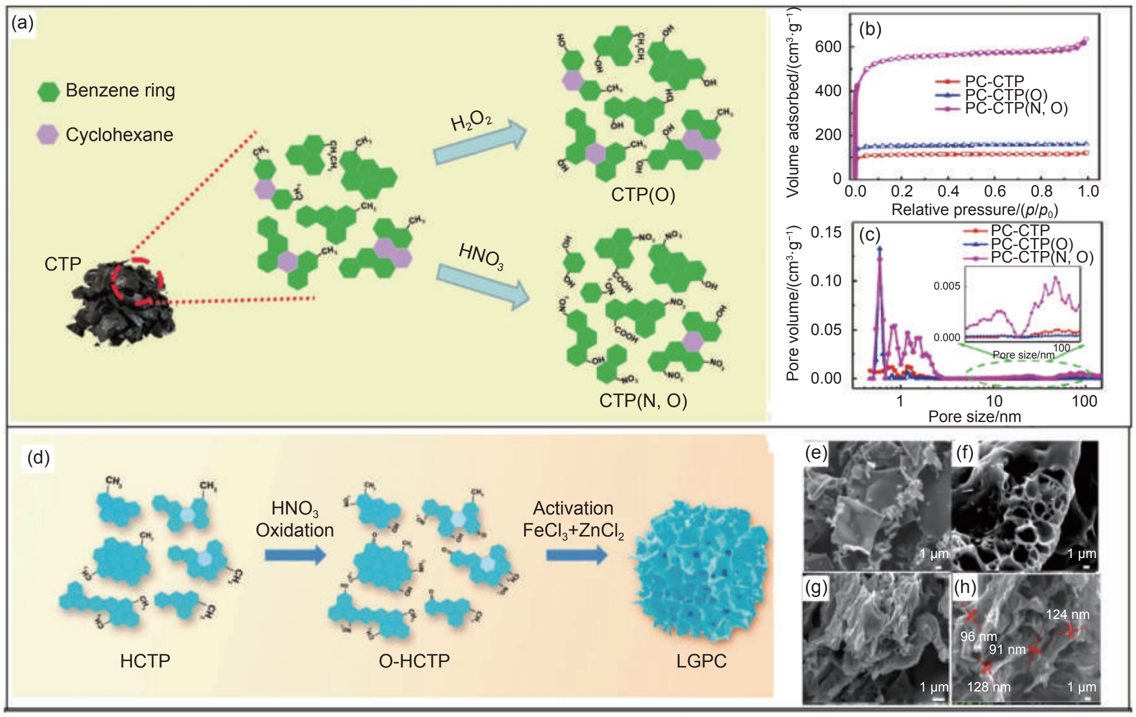

Fig. 3 (a) Schematic diagram for adjusting hydrophily and aromaticity strategy[50], (b) the N_2 sorption isotherm and (c) pore size distribution of sample treated by various oxidants. Copyright 2022 Elsevier Ltd. (d) Schematic diagram of LGPC[51], SEM images of samples (e) without additions and with (f) $ZnCl_2$, (g) $FeCl_3$, (h) $ZnCl_2$, $FeCl_3$. Copyright 2021 Elsevier Ltd

properties of carbon products by changing the pre-oxidation temperature (Fig. 4a). As shown in Fig. 4b-c, the oxygen containing functional groups can be controlled by adjusting the temperature. A large number of oxygen-containing groups in the aromatic ring can avoid the mutual accumulation of pitch molecules to form a blocky structure. Besides, the introduction of oxygen-containing functional groups can also improve the hydrophilicity of pitch molecules. Lu et al.[55] reported an air pre-oxidation method to control the microstructure of pitch-based carbon. Usually, the pitch-based carbon materials obtained by directly pyrolyzing at high temperature show highly graphitized regular structure. But after the pitch is pre-oxid-

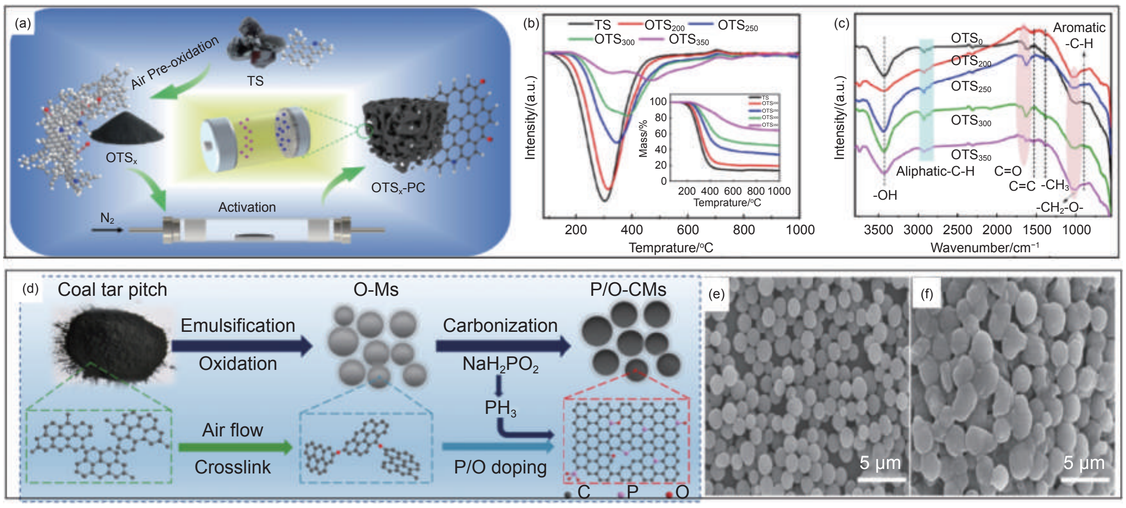

Fig. 4 (a) Schematic diagram for OTS-PC[54], (b) the thermogravimetric curve and (c) fourier infrared image of samples treated at various temperatures. Copyright 2022 Elsevier Ltd. (d) Schematic diagram of P/O-CMs[56], (e, f) the SEM images of carbon materials prepared at different temperatures. Copyright 2022 Elsevier Ltd ized at 300 °C for 3 h and then pyrolyzed at high temperature, amorphous activated carbon can be obtained. This may be attributed to the introduction of an appropriate amount of oxygen-containing functional groups on the side chain of the aromatic ring can prevent pitch molecules from melting and piling up into regular structures. Furthermore, Liu et al.[56] have synthesized P/O doped nanospheres from pitch (Fig. 4d) through pre-oxidation and emulsification. As shown in Fig. 4e-f, the morphology of the microspheres is affected by the pre-oxidation temperature. When the temperature rises to 300 °C, the microspheres appeared adherent features. After the oxidation product is mixed with sodium dihydrogen phosphate, the phosphorus/oxygen double doped microspheres with spherical structure are obtained by high-temperature pyrolysis.

3 Synthesis methods

In order to overcome the influence of inherent thermoplasticity on the structural regulation of pitch-based carbon materials, template method is developed and considered as an effective route. Generally, template method can be divided into soft template and hard template methods according to the nature of the used template[57–59]. Soft template method typically uses amphiphilic molecules as structure directing agent to assemble the precursors into the composite materials with specific structure. Then the porous materials can be obtained after the template being decomposed at high temperature or washed by solvent[60–61]. When the hard template method is employed to prepare the porous materials, the template with a specific shape or size is mixed with the precursor to form a kind of composite. As the reaction proceeds, the precursor molecules will form the macromolecules through condensation polymerization and cross-linking reaction. At the same time, the formed thermoset molecules coated on the template surface as thin layer, then the porous materials with specific structure and size are obtained after removing the template[62–63]. Because the pore structures are supported by the hard template, the formation of pores is not affected by properties of precursors.

3.1 Hard template method

Pitch is a kind of thermoplastic substances and easy to be melted, hard template method is widely used to synthesize pitch-based porous carbon materials. The general process is as follows: the pitch and the particles of hard template are firstly mixed, and then the high-temperature pyrolysis treatment is carried out. Finally, the porous pitch-based carbon material can be obtained after the template is removed. During the thermal treatment process, when the temperature rises to the softening point of pitch, the pitch begins to melt and wrap the template particles closely. As the temperature continues to rise, the pitch molecules start to be cross-linked and solidified on the surface of the template. After the pitch-based precursor is completely carbonized, porous carbon materials with specific morphology and pores can be obtained by washing away the template. As shown in Fig. 5a-b, Li et al.[64] synthesized nano rod like hierarchical porous carbon material by one-step method with pitch as raw material and magnesium carbonate nanorods as template. Similarly, Xing et al.[65] used magnesium citrate as both template and inducer, while pitch as raw material to prepare noodles like porous carbon (Fig. 5c-e). Furthermore, Xing et al.[66] also used nano calcium carbonate as a template to prepare porous carbon. They mixed calcium carbonate with pitch in tetrahydrofuran to form a uniform composite of CTP and nano calcium carbonate after the evaporation of tetrahydrofuran. During the pyrolysis process, the calcium carbonate particles are decomposed to release the carbon dioxide, at the same time micropores are formed. Moreover, as the released carbon dioxide clumps together and releases outward, it leaves large pores in the carbon matrix. The above metioned works have proved that the porous carbon materials with optimized specific surface area and pore structure can be prepared (Fig. 5f-h). Therefore, as an efficient synthesis method of carbon materials, the hard template method can precisely control the pore structure and morphology of carbon products.

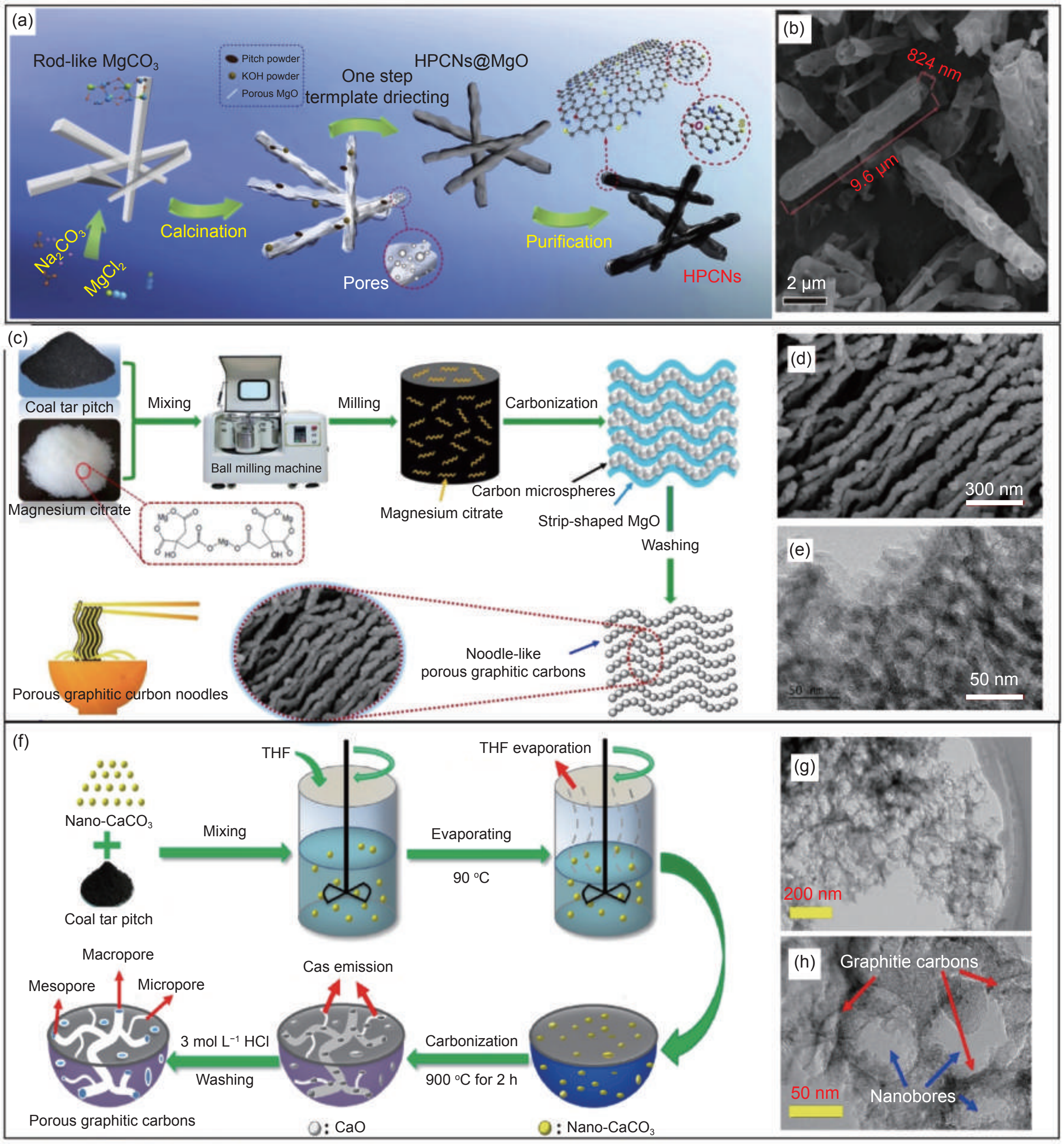

Fig. 5　(a) The illustration of the HPCNs. (b) SEM image of HPCNs[64]. Copyright 2020 Elsevier Ltd. (c) Schematic illustration of the NPGCs, (d, e) SEM images of NPGCs[65]. Copyright 2021 Elsevier Ltd. (f) The illustration of the PCs, (g, h) nTEM of PCs[66]. Copyright 2019 Elsevier Ltd

3.2　Soft template method

The commonly used soft templates are amphiphilic polymers or supramolecules (F127, P123, F108, etc.), which are self-assembled with carbon precursors to form micelles through Van der Waals force, hydrogen bonding or electrostatic interaction. In the subsequent high temperature stage, the soft template will be decomposed and depart from the carbon matrix, thus no additional removal process is required[67–68]. He et al.[69] have chosen melamine as soft template and nitrogen dopant, potassium hydroxide as activator, and CTP as carbon precursor to prepare porous carbon material. After the reactants have been mixed in solid phase and pyrolyzed, honeycomb like porous carbon is formed. Cheng et al.[70] have employed the amphiphilic effect of block copolymer P123 to prepare mesoporous carbon spheres from nitric acid treated CTP. It is found that the P123 amount has a significant impact on the microstructure of carbon materials. Wang et al.[71] have prepared a hydrogel network *via* the hydrogen bonding and conjugation between carboxylated pitch and polyacrylic acid. During pyrolysis, the gas generated from the decomposition of polyacrylic acid (PAA) leaves pores on the surface of molten pitch. The carbon dioxide and water generated at high temperature will etch the carbon skeleton and introduce the micropores in carbon by the reactions as follows: CO_2+C=2CO, H_2O+C=CO+H_2. Thus, the carbon material obtained with PAA shows a larger SSA and wider PSD compared with the sample without PPA.

3.3 Molten salt method

In order to avoid the use of acid and alkali that pollute the environment in the process of removing templates. Researchers have spent lots of attentions to find green methods for preparing porous carbon. In recent years, molten salt method is widely used in the synthesis of inorganic materials including carbon materials[72–74]. For the binary inorganic eutectic salt, it can be melted at a lower temperature to provide a uniform liquid reaction medium for the reactants (Fig. 6a-c). Besides, the molten salts can also act as structure directing agents to form special structures. For example, CTP with softening point of 85 °C have been selected as carbon precursor, NaCl/$ZnCl_2$ binary inorganic eutectic salt with eutectic point of 275 °C as

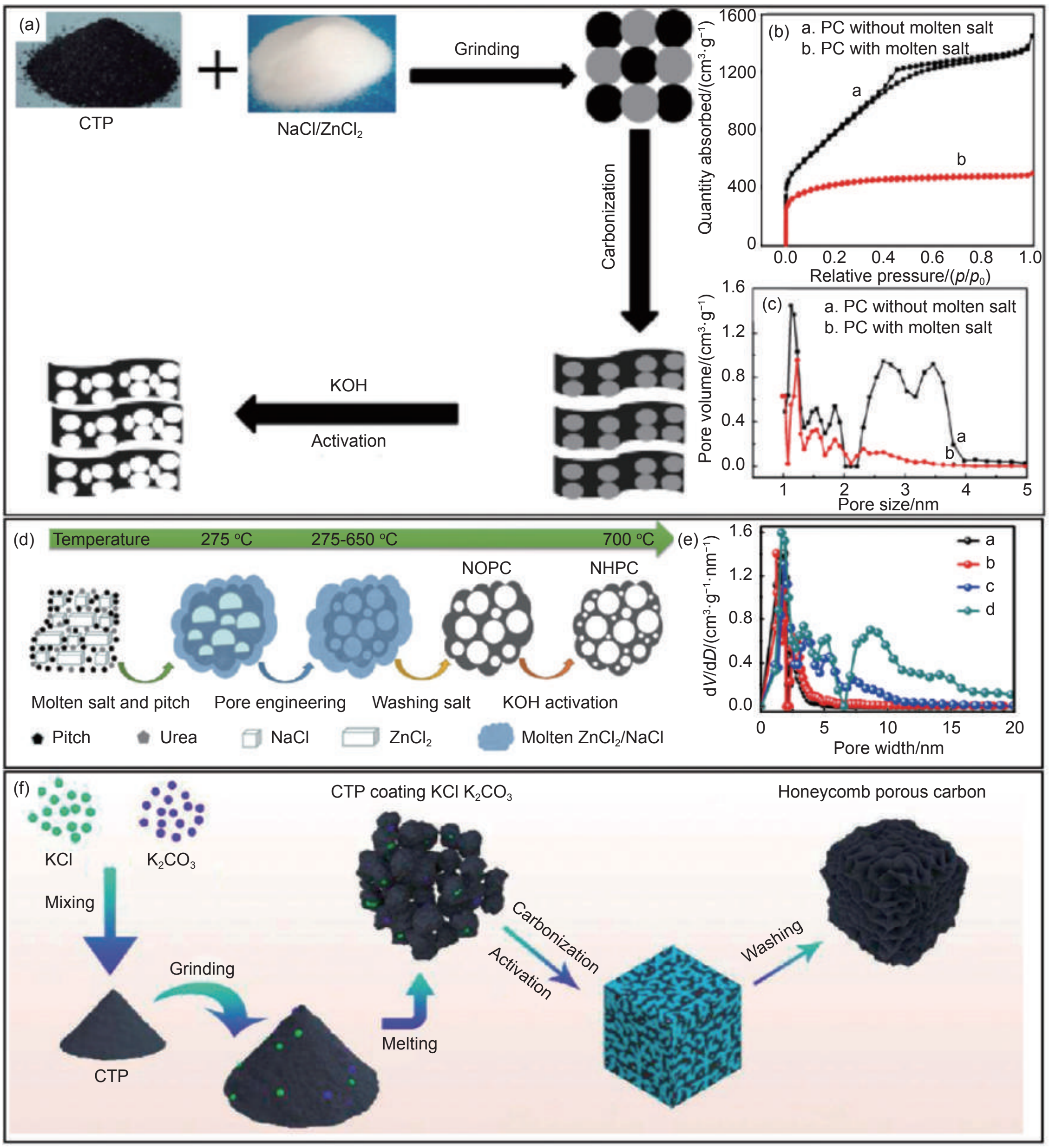

Fig. 6 (a) The illustration of the HPC[75]. (b) N_2 sorption isotherms and (c) pore size distribution of PCs. Copyright 2021 Elsevier Ltd. (d) The illustration of the NHPC and (e) pore size distribution of NHPC[76]. Copyright 2022 Elsevier Ltd. (f) The illustration of HPC[77]. Copyright 2022 Elsevier Ltd the reaction medium and template to obtain the hierarchical porous carbon with high specific surface area (2 984 m^2 g^{-1}) after being activated by potassium hydroxide[75]. It is found that the introduction of molten salt into the synthesis process can significantly accelerate the polymerization rate of pitch molecules and increase the mesoporous volume in the carbon materials (Fig. 6d-e). In order to further improve the pore structure of carbon materials, the urea has been introduced into the above-mentioned system[76]. During pyrolysis, urea can be used as foaming agent to blow molten pitch, leading to looser structure. It can also introduce nitrogen atoms into the carbon skeleton. The results reveal that the resultant carbon materials show ultra-high specific surface area and pore volume. Ren et al.[77] have selected KCl/K_2CO_3 with eutectic point of 631 °C as flame retardant and activator to prepare pitch-based carbon. Honeycomb carbon materials doped with N and O are obtained by one-step pyrolysis in air. The eutectic salt system in the molten state can protect the pitch from etching by excessive oxygen in the air, and the molten K_2CO_3 can better contact the molten pitch and improve the activation efficiency of potassium carbonate. Thanks to the above advantages, the prepared porous carbon shows a regular honeycomb porous structure. At the same time, it shows excellent electrochemical performance (Fig. 6f). Liu et al.[78] have used pitch with softening point of 80 °C as raw material, NaCl/KCl (eutectic point, 650 °C) system as template and structure directing agent to prepare graded porous carbon. The research shows that under the same reaction conditions, the sample after pyrolysis treatment changes from hierarchical porous structure to blocky structure when only LiCl/KCl (eutectic point, 353 °C) molten salt system is used to replace NaCl/KCl. The obvious microstructure change reveals that different molten salt systems will have an important impact on the micro morphology of carbon products. Therefore, the structure and pore distribution of pitch-based porous carbon materials can be controlled by changing the system of molten salts.

4 Applications

Electrodes are important components for energy storage devices, and pitch-based carbon with nanostructures are promising electrode materials. The applications of pitch-based porous carbon in energy storage are summarized in Table 1.

4.1 Supercapacitors

Carbon-based SCs have attracted extensive attention due to their high power density, excellent cycle stability, wide operating temperature and other advantages. However, relatively low capacitance and energy density have limited their widespread applications[79–80]. There are a lot of references report that the electric double-layer capacitor (EDLC), as the main contributor for the carbon-based SCs' capacity, arises from the reversible adsorption/desorption of electrolyte ions on the electrode surfaces, and carbon materials with various morphologies have been designed and synthesized, such as carbon nanotube, carbon nanosphere and porous carbon, etc. As another component of capacity, pseudocapacitors relies on the reversible oxidation/reduction reaction of the heteroatoms on the carbon, and its contribution for capacity is also needed to be considered. Therefore, pore engineering and doping strategies have been widely used to improve the performance of carbon-based SCs.

4.1.1 Pore structure

The capacitance value of carbon-based SCs mainly depends on the SSA of the carbon electrode materials. However, the relationship of capacitance and SSA is nonlinear. The reason may be that the pore structure also shows an important effect for performances of carbon based SCs. Generally, micropores are the main contributor for carbon materials' SSA, which can boost the electrochemical performances of carbon based SCs. However, the micropores are not easy contact with electrolyte ions due to their small size (< 2 nm). Fortunately, the mesopores and macropore can act as highway for ions transport due to their large pore diameter. Thus, carbon materials with hierarchical porous structure have been designed and prepared recently. Xue et al.[81] have proposed a pitch based porous carbon prepared by mixing soft and hard car-

Table 1 The applications of pitch-based carbon materials

Materials	Carbon precursors	Device type	Capacity	Ref.
HPCs	Coal tar pitch	Supercapacitor	356.8 F g^{-1} at 0.5 A g^{-1}	[41]
PCs	Coal tar pitch	Supercapacitor	602 mF cm^{-2} at 4 mA cm^{-2}	[42]
PCs	Coal tar pitch	Supercapacitor	380 F g^{-1} at 2 A g^{-1}	[43]
HPCNs	Pitch	Supercapacitor	221 F g^{-1} at 1 A g^{-1}	[65]
NPGCs	Coal tar pitch	Lithium-ion battery	1157 mA h g^{-1} at 0.05 A g^{-1}	[65]
NPGCs	Coal tar pitch	Lithium-ion battery	707 mA h g^{-1} at 0.05 A g^{-1}	[66]
PC	Coal tar pitch	Supercapacitor	327 F g^{-1} at 1 mV s^{-1}	[67]
NHPC	Coal tar pitch	Supercapacitor	341 F g^{-1} at 0.5 A g^{-1}	[71]
CKK	Coal tar pitch	Supercapacitor	309.5 F g^{-1} at 0.5 A g^{-1}	[72]
NSC	Coal tar pitch	Potassium-ion battery	359 mA h g^{-1} at 0.1 A g^{-1}	[73]
HPCs	Coal tar pitch	Supercapacitor	221 F g^{-1} at 0.05 A g^{-1}	[76]
HPCs	Coal tar pitch	Supercapacitor	292 F g^{-1} at 1 A g^{-1}	[77]
PC	Coal tar pitch	Supercapacitor	318 F g^{-1} at 0.5 A g^{-1}	[50]
LGPC	Coal tar pitch	Supercapacitor	337 F g^{-1} at 0.5 A g^{-1}	[51]
3DPCs	Coal tar pitch	Supercapacitor	306 F g^{-1} at 0.5 A g^{-1}	[52]
OTS-PC	Coal tar pitch	Supercapacitor	298 F g^{-1} at 0.5 A g^{-1}	[54]
DC	Pitch	Sodium-ion battery	300.6 mA h g^{-1} at 0.1 A g^{-1}	[55]
P/O-MC	Coal tar pitch	Potassium-ion battery	352 mA h g^{-1} at 0.05 A g^{-1}	[56]
HPC	Pitch	Supercapacitor	340 F g^{-1} at 0.5 A g^{-1}	[81]
HPCs	Coal tar pitch	Supercapacitor	321.5 F g^{-1} at 0.5 A g^{-1}	[82]
NHCA	Petroleum pitch	Supercapacitor	307 F g^{-1} at 0.05 A g^{-1}	[83]
N, O-PC	Coal tar pitch	Supercapacitor	532.5 F g^{-1} at 0.5 A g^{-1}	[84]
HPC	Soft pitch	Lithium-ion battery	1251 mA h g^{-1} at 0.1A g^{-1}	[89]
MCMB	Coal tar pitch	Lithium-ion battery	639 mA h g^{-1} at 0.04A g^{-1}	[90]
PC	Coal tar pitch	Sodium-ion battery	278 mA h g^{-1} at 0.1A g^{-1}	[92]
NCFs	Pitch	Sodium-ion battery	341 mA h g^{-1} at 0.1A g^{-1}	[93]
HCs	Pitch	Potassium-ion battery	321.9 mA h g^{-1} at 0.5 A g^{-1}	[94]
NPPC	Coal tar pitch	Potassium-ion battery	240 mA h g^{-1} at 0.05 A g^{-1}	[95]

bon precursors for SCs (Fig. 7a). During the process of carbonization, pitch melts and wraps on the surface of hard carbon that could be used as a template. The porous carbon material is obtained after being activated by potassium hydroxide. The SSA and pore structure of carbon materials are adjusted by changing the amount of biomass added in the precursor, thus controlling the electrochemical performance of SCs. When the mass ratio of pitch to chaff is 1 ∶ 1, the prepared porous carbon has a high SSA of 2 996 m^2 g^{-1}. The assembled SC shows high capacitance of 340 F g^{-1} at a current density of 0.5 A g^{-1} and excellent electrochemical magnification performance. Liu et al.[82] have applied a double roles salt ($NaHCO_3$) as pores creator to synthesis hierarchically porous carbons (HPCs). The optimal HPC shows high SSA and large total pore volume. Thus, the carbon material with multi-size pores shows an excellent electrochemical performance. The device assembled by HPC can achieve a high energy density of 50 Wh kg^{-1} at power density of 750 W kg^{-1} (Fig. 7b). Because the traditional potassium hydroxide activation method is cumbersome and harmful, Guan et al.[83] have used potassium citrate as the activator and *in situ* template to prepare pitch based porous carbon nano layers as electrode materials for SCs (Fig. 7c). The porous carbon has a large SSA, suitable pore structure and sheet structure. Impressively, in the potassium hydroxide electrolyte, the energy density of the device can reach to 10.7 Wh kg^{-1}.

4.1.2 Heteroatom doping

Introducing heteroatoms into carbon matrix is another effective strategy to increase the capacitance of porous carbon electrode. The heteroatoms doping can also modify the carbon materials' surface capability (improving the infiltration, reducing the resistance and introducing pseudocapacitor). Therefore, many doped pitch-based porous carbons are prepared. For ex-

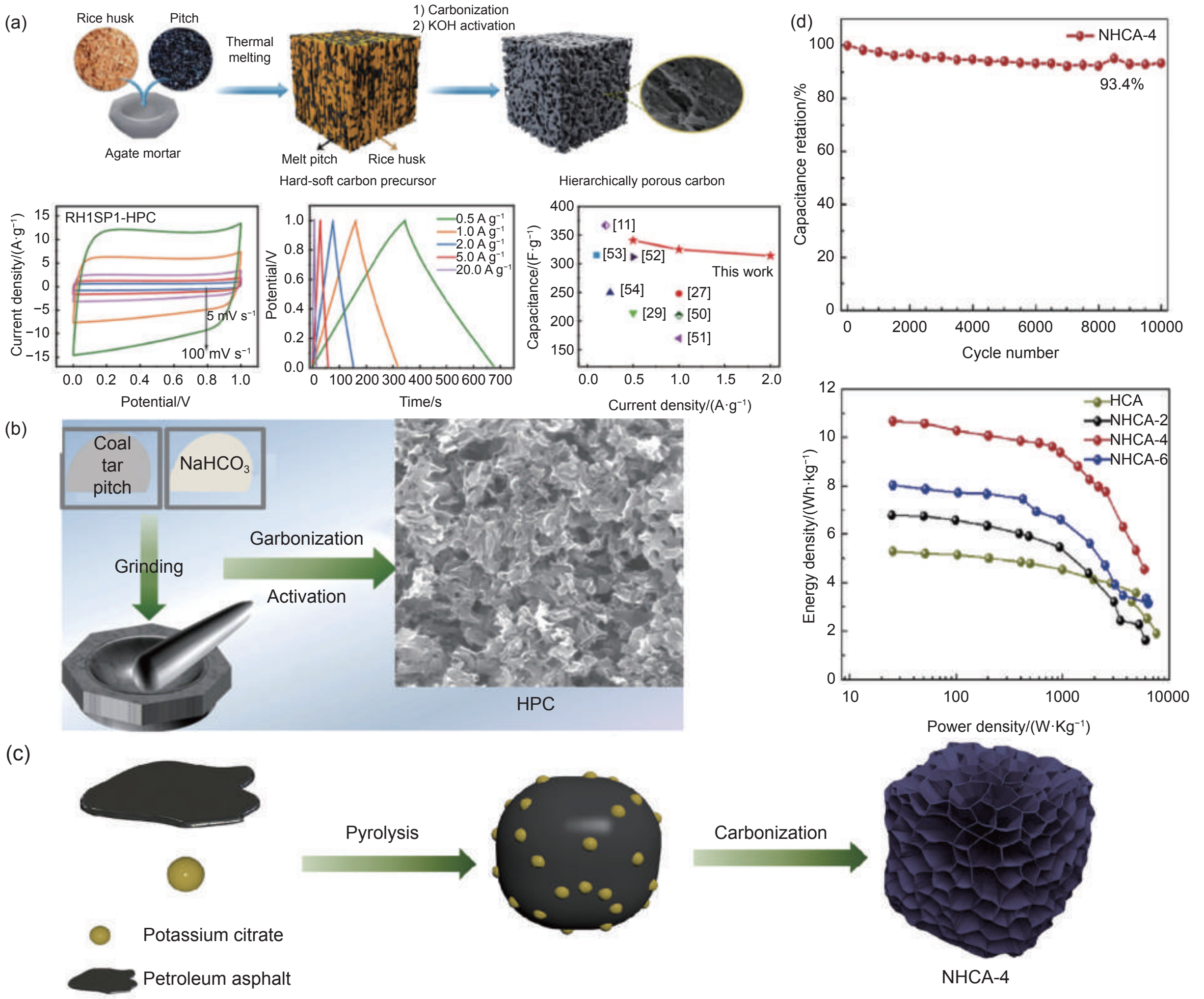

Fig. 7　(a) Schematic diagram for HPCs and electrochemical performance of cell based by RH1SP1-HPC[81]. Copyright 2021 American Chemical Society (b) Graphic abstract of the hierarchically porous carbons[82]. Copyright 2023 American Chemical Society. (c) Schematic diagram for NHCA-4 and (d) electrochemical performance of cell based by NHCA-4[83]. Copyright 2019 Elsevier Ltd

ample, Cao et al.[84] have prepared the N, O-doped porous carbon with high specific capacitance from the pitch. Due to the combined action of strong pore forming effect of potassium hydroxide and the introduction of N to optimize the electronic structure of carbon network, the N, O-doped porous carbon electrode shows a high C_g value of 315.5 F g^{-1} at 0.5 A g^{-1} in a two electrodes system, and a high energy density of 43.8 Wh kg^{-1}. Similarly, Yin and co-workersup[85] have prepared a N/O self-doped porous carbon by using coal tar pitch and fluid catalytic cracking oil as precursor, $Ni(NO_3)_2$ and KOH as catalysts and pore creator, respectively. Benefitting from the large SSA (2 254 m^2 g^{-1}) and the effect of N, O co-doping, the optimal N/O doped porous carbon shows high specific capacitance of 368 F g^{-1} at 0.5 A g^{-1} and excellent rate capability (270 F g^{-1} at 20 A g^{-1}). Furthermore, the assembled device displays a maximum energy density of 27.45 Wh kg^{-1} at 253 W kg^{-1} in 1 mol L^{-1} Na_2SO_4 electrolyte. A 3D N/O co-doped porous carbon has been prepared by one-pot method. The result of SEM suggests the morphology of carbon materials can be controlled by the addition of potassium hydroxide. Because of the continuous hierarchical porous structure and high N content (8.22%), the obtained materials display exceptional specific capacitance of 302 F g^{-1}, excellent rate capability and superior cycling stability.

4.2　Alkali metal ion batteries

For alkali metal-ion batteries, they have drawn attentions due to their ultrahigh theoretical capacity and energy density. However, the slow electrode kinetics makes the batteries show terrible rate capability. Carbon materials can be used as anode materials of ion batteries due to their excellent conductivity, high stability, adjustable pore structure and low cost[86]. Generally, to address the slow electrode kinitics, some key issues should be considered during the design process, such as hierarchical pore structure containing micro-, meso- and macro-pores, which can not only ensure sufficient active site, but also ensure the rapid transport of ions to enhance the electrochemical properties of batteries. Preparing unique structural carbon materials, such as 2D carbon nanosheets, porous carbon nanosphere and porous carbon, will shorten the transmission distance of ions in electrode materials. The surface property of carbon materials also has an important effect to their performances, which can improve both the capacity and rate capability of batteries *via* redox reaction and the wettability of electrode surface.

4.2.1 Lithium-ion batteries

For lithium-ion batteries (LIBs), the graphite electrode shows a low capacity that hinders its further applications. Carbon materials with various morphologies (carbon nanosheet, carbon microsphere, carbon nanotube and porous carbon) have been synthesized to overcome this disadvantage[87–88]. A new strategy for synthesizing pitch based porous carbon sheets is reported by the higher authorities (Fig. 8a). As the main component of the shell is calcium carbonate, the author ingeniously designed to use the shell as a template and activator to prepare carbon nano sheets. Thanks to the 2D nanosheet structure and hierarchical pore structure of carbon materials, lithium ions can move rapidly in carbon materials. Therefore, LIBs assembled by carbon nano chips had a high reversible capacity of 1 251 mAh g^{-1} and excellent magnification performance[89]. Parkash et al.[90] have prepared a spherical carbon material by direct pyrolysis of the CTP without activators and templates. During the pyrolysis process, the polycyclic aromatic hydrocarbons will generate larger molecular structure under the action of free radicals, and the large molecular structure is the basis for the formation of mesophase asphalt. Furthermore, the mesophase asphalt can format the spherical carbon materials under the optimization of the pyrolysis parameters. The optimized sample exhibites a high capacity of 336 mAh g^{-1} and after 60 cycles with capacity retention of 60%.

4.2.2 Sodium-ion batteries

Compared with LIBs which have been successfully commercialized, the sodium-ion batteries SIBs possess competitive advantages of low cost and abundant raw materials. Besides, the Na^+ as the electron carrier can encourage researchers to explore new oxidation reaction mechanisms. Specifically, the aluminum foil can replace copper foil as current collector, because Na will not react with aluminum when the battery is in an over discharged state[91]. Carbon materials are often used as the cathode materials of SIBs. But the CTP-based carbon materials always show a high graphic structure which is obstructed the adsorption of Na^+ leading to a low capacity. In order to prevent the pitch-based carbon products from forming highly graphitized structure, Qi et al.[92] have prepared the carbon materials for SIBs by adding curing agent ($Mg(NO_3)_2$) (Fig. 8b). In the pyrolytic process, the $Mg(NO_3)_2$ will decompose into gas and magnesium compounds, which can impede the pitch to soften and form regular structures. Hence the optimal carbon materials shows a significant performance improvement compared to the pitch-based carbons without curing agent. The assembled half-cell possesses a high reversible capacity of 278 mAh g^{-1} (platform capacitance value accounts for about 61%) and a superior rate capability (278 mAh g^{-1} at 0.1 C, 74 mAh g^{-1} at 2 C). The full-cell still shows desirable electrochemical performance. The flexible energy storage device as an important part of energy storage field is also drawing many attentions of researchers. Wang et al.[93] have successfully synthesized a free-standing flexible Na^+ anode from CTP/polyacrylonitrile by electrospinning. The NH_3 treatment is introduced to enlarge the layer distance of carbon and control the microstruc-

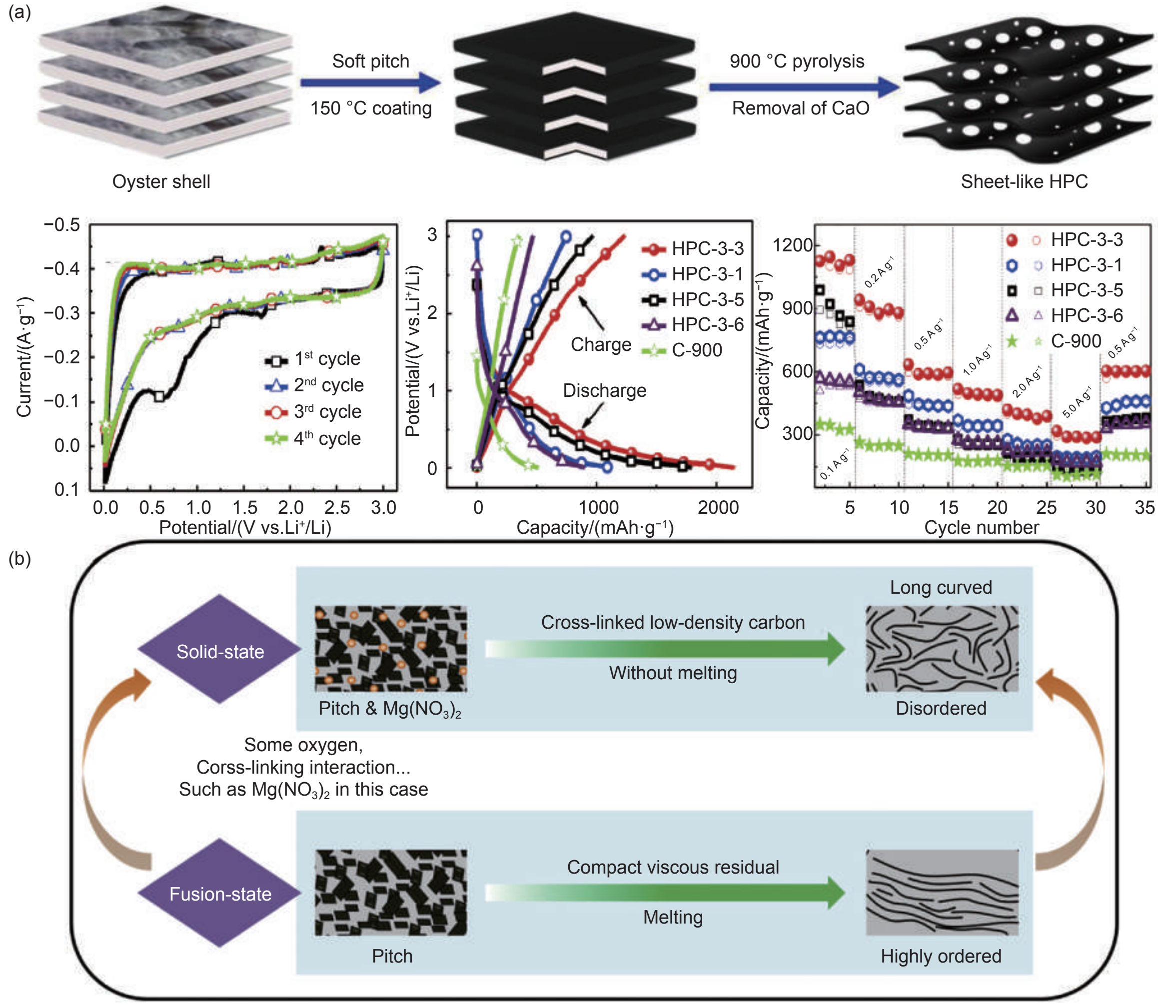

Fig. 8　(a) Schematic diagram for sheet-like HPCs and electrochemical performance of cell[89]. Copyright 2018 Elsevier Ltd. (b) Schematic diagram for carbon materials[92]. Copyright 2020 Elsevier Ltd

ture of carbon materials. The carbon materials shows an outstanding flexibility, and the half-cell assembled by carbon exhibits a superior Na^+ storage behavior and a high initial Coulombic efficiency of 53.4%. This carbon material also shows a high capacity of 314 mAh g^{-1} at 0.1 A g^{-1}, an excellent rate capability (197 mAh g^{-1}at 2 A g^{-1}) and a long cycle life (capacity retention of 100% after 10 000 cycle).

4.2.3　Potassium-ion batteries

Compared with lithium, potassium is rich in Earth's crust, so the potassium-ion batteries (KIBs) are also considered as an important device in the field of energy storage. Like other energy storage devices, carbon materials are usually used as anode in KIBs. Recently, Yin et al.[94] have prepared hard carbon materials by co-carbonizing the phenolic resin and pitch to use in SIBs and KIBs (Fig. 9a). The optimized sample exhibits a high reverse capacity of 349.9 mAh g^{-1}, extremely excellent rate performance (145.1 mAh g^{-1} at 20 A g^{-1}), and ultrahigh cycle stability (capacity retention of 94.5% after 2 500 cycles at 1 A g^{-1}) in sodium ion battery. In addition, the HC-0.2P-1000 delivered an excellent potassium storage performance (321.9 mAh g^{-1}). The full cell exhibits a high energy density of 251.1 Wh kg^{-1} and excellent stability with a capacity retention of 73.3% after 450 cycles at 1 A g^{-1}. By using CTP as carbon source, NaCl as a hard template and ammonium polyphosphate as N and P source, Ma et al.[95] have adopted a simple and effective one step carbonization strategy to prepare N, P dual-doped CTP-based porous carbons (NPPC) as the anode material of high-rate battery

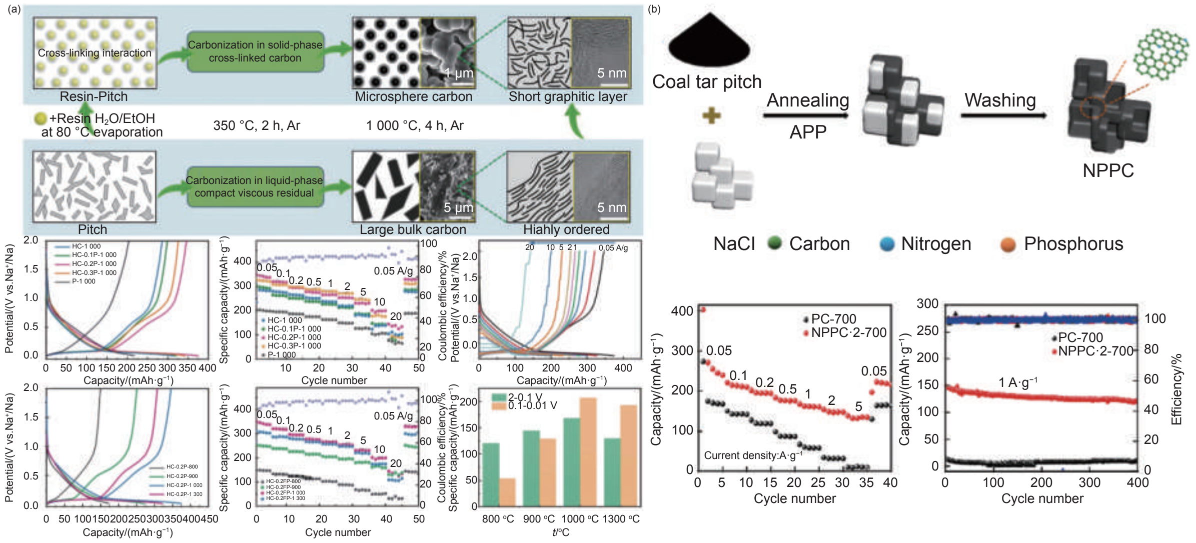

Fig. 9 (a) Schematic diagram for carbon materials from pitch and the electrochemical performances for SIBs[94]. Copyright 2021 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) The schematic diagram for NPPC and the electrochemical performances for the cell based on NPPC[95]. Copyright 2021 Elsevier Ltd

(Fig. 9b). Under the action of salt template, the NPPC shows a mesoporous dominated structure, which is conducive to ion transmission. The optimal NPPC electrode displays an excellent rate performance with a capacity of 240 mAh g^{-1} at 0.05 A g^{-1} (133 mAh g^{-1} at 5 A g^{-1}). As expected, the optimal NNPC also exhibits outstanding cycle stability. The capacity can maintain 81.8% of initial capacity even at a high current density of 1 A g^{-1} after 400 cycles.

5 Conclusion

According to the above-mentioned research advances, carbon materials derived from pitch have proved to possess extensive applications in the field of energy storage including supercapacitors and alkali metal ion batteries, due to their excellent physical and chemical inertness. However, using pitch as carbon precursor still faces the following problems which need to be well addressed: (1) The complex chemical composition of pitch makes it difficult to precisely control the structure of porous carbon product. (2) The inherent thermal plasticity of pitch makes pitch tend to form blocky structure during heating process. (3) The main components of CTP are polycyclic aromatic hydrocarbons and their derivatives. Therefore, large conjugated structure of pitch molecules drives pitch to form a stacking structure, which is not conducive to the formation of pores, and less active sites on pitch molecules make them difficult to be cross linked with other compounds. To this end, the following methods are summarized in this review to regulate the structure of pitch-based carbon: solvent partition method, which divides the complex components of pitch into units with similar structures, so that researchers can more effectively regulate the structure of single component of pitch. However, toluene, quinoline and other toxic organic solvents are commonly used in solvent segmentation. Due to the thermoplasticity of pitch, template method can well control the structure and morphology of pitch-based porous carbon materials when it is used to synthesize porous carbon materials. In the template methods, the removal process of hard template is more complex, and the price of soft template is expensive, which is difficult to apply to large-scale production. The oxidation method can improve the hydrophilicity of pitch by introducing functional groups into the aromatic structure of pitch molecules, and can also increase the reactive sites of pitch, which can make pitch more easily react with other reagents. However, the oxidants such as nitric acid, hydrogen peroxide and potassium permanganate may bring the structure defects and environmental concern. As for the energy storage applications, supercapacitors possess high power density and long cycle life, while they are restricted by the low energy density. Thus, the efforts should be aimed at preparing advanced carbon materials to meet the demand of high energy density. On the other side, the ions batteries always display high energy density but featuring poor cycle stability and low power density. Therefore, when carbon materials are used as electrode materials, these issues should be concerned.

Currently, the development prospects of pitch-based carbon materials carbon materials are already obvious. However, there are still issues on the aspects such as the precise regulation of structure for pitch-based porous carbon material and the determination of pitch's composition components. Although various methods can be used to prepare carbon materials with different morphologies from coal tar pitch, these methods to convert pitch into high value-added products simply are still scarce, which limits the pitch's high value application large scalely. Obtaining more detailed information for the formation process of pitch-based carbon will be helpful to understand the carbon material's formation mechanis, which is facilitate to design more reasonable synthesis strategy. Therefore, more advanced *in-situ* characterization methods will be combined to conduct the detailed information. We look forward to new opportunities and progress in energy storage and conversion for pitch-based carbon materials.

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