



Review article



Present development and future perspectives on biowaste-derived hard carbon anodes for room temperature sodium-ion batteries

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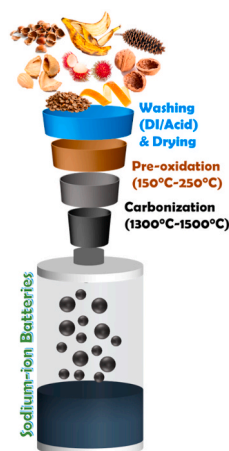
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HIGHLIGHTS

- Hard carbon is the best candidate as an anode material for sodium-ion batteries.
- This review shares challenges and opportunities of hard carbon materials.
- We highlight bio-waste-derived hard carbons for practical applications.
- Developing stable anode materials is key for commercializing sodium-ion batteries.

GRAPHICAL ABSTRACT



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ABSTRACT

Sodium-ion batteries are regarded as an affordable alternative to commercial lithium-ion batteries in energy storage systems because of their abundant resources and comparable energy storage capabilities. Hard carbon is a prospective anode material to consider for the commercialization of sodium-ion batteries due to its promising electrochemical performance and the possibility of using renewable resources of bio-waste to obtain hard carbon. However, numerous disadvantages, including low initial coulombic efficiency and voltage hysteresis, continue to

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constrain the use of hard carbon in sodium-ion batteries. Various strategies have been attempted to address these challenges to transfer present promising research opportunities into practical applications. This review provides recent insights on bio-waste-derived hard carbons, which are classified into different types of hard carbon precursors, the effect of carbonization temperature and doping on the physical characteristics, and the variation in the property of hard carbon under different synthetic parameters is directly correlated with sodium storage process. We discuss the associated sodium storage mechanisms in-depth. This work also provides a future perspective on bio-waste-derived hard carbons and the feasibility of their practical utilization in room temperature type low-cost sodium-ion batteries.

1. Introduction

Energy storage systems (ESSs) are increasingly important, particularly in smart networks and electric vehicles. Since Sony's successful commercialization in 1991, lithium-ion batteries (LIBs) play a pivotal role in advanced energy storage systems and the development of various portable electronics for daily application due to their high-power, high-energy density, and long-term stable cyclability [1–3]. However, industrial production of LIBs has environmental and ecological problems: unevenly distributed and limited land-based lithium reserves and serious ecological hazards associated with disposal and recycling (caused by toxic components) [4–6]. Accordingly, the challenge is to find new alternatives powered by economical and abundant materials [7–9].

In this case, sodium-ion-based batteries may offer several attractive qualities. Abundant raw materials based on sodium, which is the fourth most abundant element on earth, can lower the price of batteries. Accordingly, inexpensive sodium can be used as a charge carrier for sodium-ion batteries (SIBs). Indeed, the research on LIBs and SIBs have initiated in the 1970s; however, the development was accelerated toward LIBs due to the easy handling of moisture-sensitive lithium-based materials and the high energy density of LIBs relative to SIBs. Recent pressure on the price of LIBs regarding lithium with a limited reserve and a surge of cobalt and nickel prices urges us to revisit the forgotten SIBs [10–12]. In addition, the recent splendid development of science and technology enables reinvestigation the moisture-sensitive sodium-based materials through various the-state-of-the-art equipment. Most of all, sodium has similar chemical and physical properties in comparison with lithium due to its location in the same group of the periodic table [13].

For the element of sodium, the molecular weight of sodium (23 g mol^{-1}) is heavier than lithium (6.9 g mol^{-1}), and sodium has an electrode potential (-2.71 V vs standard hydrogen electrode (SHE)) less electroactive than lithium (-3.04 V vs SHE). This means that the corresponding operation voltage and energy density of sodium-based materials are always lower than those of lithium system, although the same transition metal elements are available in both systems. In addition, the large ionic radius of sodium ($1.02 \text{ \AA}$) relative to that of lithium ($0.76 \text{ \AA}$) causes successive phase transitions as extraction and insertion of the large sodium ions are progressed, of which such tendency is less evident in the lithium system. These are considered to be one of the possible reasons for the degradation of cell performance, which should be circumvented for the practical application of SIBs [2,14].

Notwithstanding, Faradion, Tiamat, and Hi-Na, have announced their revolutionary technologies for the production of SIBs [15]. In 2018, 12 Ah-class SIBs full cells from Faradion's company demonstrated a maximum energy density of 140 Wh kg^{-1} , comparable to commercially available $\text{LiFePO}_4/\text{graphite}$ systems ($140\text{--}175 \text{ Wh kg}^{-1}$) [16]. Recently, "CATL", the largest battery manufacturer in China, first introduced commercial SIBs. This cell has an energy density of 160 Wh kg^{-1} and can completely charge within 15 min at room temperature. More surprisingly, the sodium-ion cell retains more than 90% of its capacity even at a low temperature (-20°C). An important feature is the use of in-house hard carbon as the anode material for CATL's SIBs, of which the feature of hard carbon has a unique porous structure that is

capable of abundant sodium-ion storage, fast diffusion of sodium ions, and excellent cycle performance [17].

The development of highly efficient and stable electrode material is so important for accelerating the commercialization of SIBs [18–24]. According to numerous works in the field of SIBs, main components such as cathodes [25–31], anodes [32–35], electrolytes [36–39], and their associated mechanisms have been intensively investigated. Nevertheless, developing stable anode materials for SIBs still remains a challenging task. It should be emphasized that highly reversible charge capacity, outstanding rate performance, and extended cycle life are all key requirements for advanced anode materials. In the case of LIBs, "graphite" is a reliable and dominant anode material for LIBs due to its abundance, low cost, and non-toxicity. Many studies pointed out that, in comparison with lithium, it is difficult to incorporate sodium ion into graphite because the graphite interlayer distance is small to host sodium ion (its radius is $\sim 36\%$ larger than lithium), hence, the adoption of graphite is substantially not feasible for SIBs [40]. Numerous efforts have been made for searching rational anodes for SIBs, which can be divided into four categories: carbonaceous materials, metal sulfides, transition metal oxides, and alloys [41]. Most of them face difficulties hosting sodium ions because the large sodium ions result in irreversible capacities during repeated de-/sodiation. In addition, the main issue of alloy materials is the huge volume expansion during cycling [42]. Among them, carbonaceous materials deliver reasonable capacities as active anode materials for SIBs; however, low initial coulombic efficiency and low electrical conductivity are the main issues to be urgently resolved [43]. Metal oxide and sulfide have insufficient electric conductivity in comparison with carbonaceous materials, such that they are usually composited with carbon-based material to supplement the conductivity [44]. In their midst, carbonaceous materials are recognized as the most promising anode materials for implementing the commercialization of SIBs, given their electrochemical characteristics.

Amongst carbonaceous materials, hard carbon (HC) is believed to be the cutting-edge anode material for SIBs. HCs are the non-graphitized form of carbon materials and are characterized by randomly distributed layers of graphitic sheets [41,51–53]. This can be explained by strong cross-linked structures or C-O-C covalent bonds in the structure, inheriting an extended interlayer distance of about $0.37\text{--}0.42 \text{ nm}$: short-range domains, large pores, and defects [43]. Azuma et al. categorized the microcrystalline structure of HCs into two types: well-stacked and not-well-stacked structures [54]. In LIBs, HCs with a microcrystalline structure consisting of not well-stacked layers often allow more Li^+ ions to be accumulated in HCs, demonstrating a high specific capacity than graphite ($400\text{--}1000 \text{ mAh g}^{-1}$ vs. 372 mAh g^{-1}) [54]. Regarding electrochemical performance, HC is the first active anode material that has reached productivity in SIBs. So far, relatively high capacity ($\sim 350 \text{ mAh g}^{-1}$), high conductivity, and low operating potential ($\sim 0 \text{ V}$ vs. Na^+/Na) make it to be one of the promising anode materials for SIBs (Fig. 1a and b). In addition, HCs are attractive due to their abundance and cost-effectiveness, and, more importantly, the material can be derived in an inexpensive way from biowastes or bio-resources. The randomly closed pores between the graphitic crystallites allow the formation of more defects and larger interlayer spacing in the structure, which can endow the diffusion pathways of sodium ions and sodium storage sites [55].

Many studies successfully experimented with HC, however, in-depth understanding behind good electrode performance needs to be further elucidated. So far, there are numerous proposed sodium storage mechanisms due to the complexity of the structure of hard carbons, and various synthesis techniques or precursors offer diverse structural features. Moreover, irreversible capacity loss (ICL) in the initial charging process is another concern to be resolved. Most likely, irreversibly trapped sodium ions in the graphene layers cannot diffuse toward the cathode, resulting in low initial coulombic efficiency (ICE <80%). As a result, the surface functional groups and defects cause undesired side reactions to deteriorate cell performance, in comparison with the ICE values of graphite (85–95%) [56]. Accordingly, it is important to understand from synthesis to mechanism for Na^+ uptake into the HCs: representatively, for rationally designed high-performance HC

materials, a thorough awareness of the sodium storage mechanism, ion transfer process, and solid electrolytic interphase (SEI) structure.

This review aims to provide a comprehensive summary on recent research advances of biowaste-derived HC materials for SIBs, highlighting the sodium storage mechanism, the classification of biowaste precursors for the synthesis of HC, as well as the effect of carbonization temperature and heteroatom doping on HC in terms of physical properties and electrochemical performances. Based on these fundamental insights, we suggest future perspectives on the performance enhancement of HCs through rational design. In general, this study can provide interest and consideration in the field of HC for rechargeable ESSs beyond SIBs.

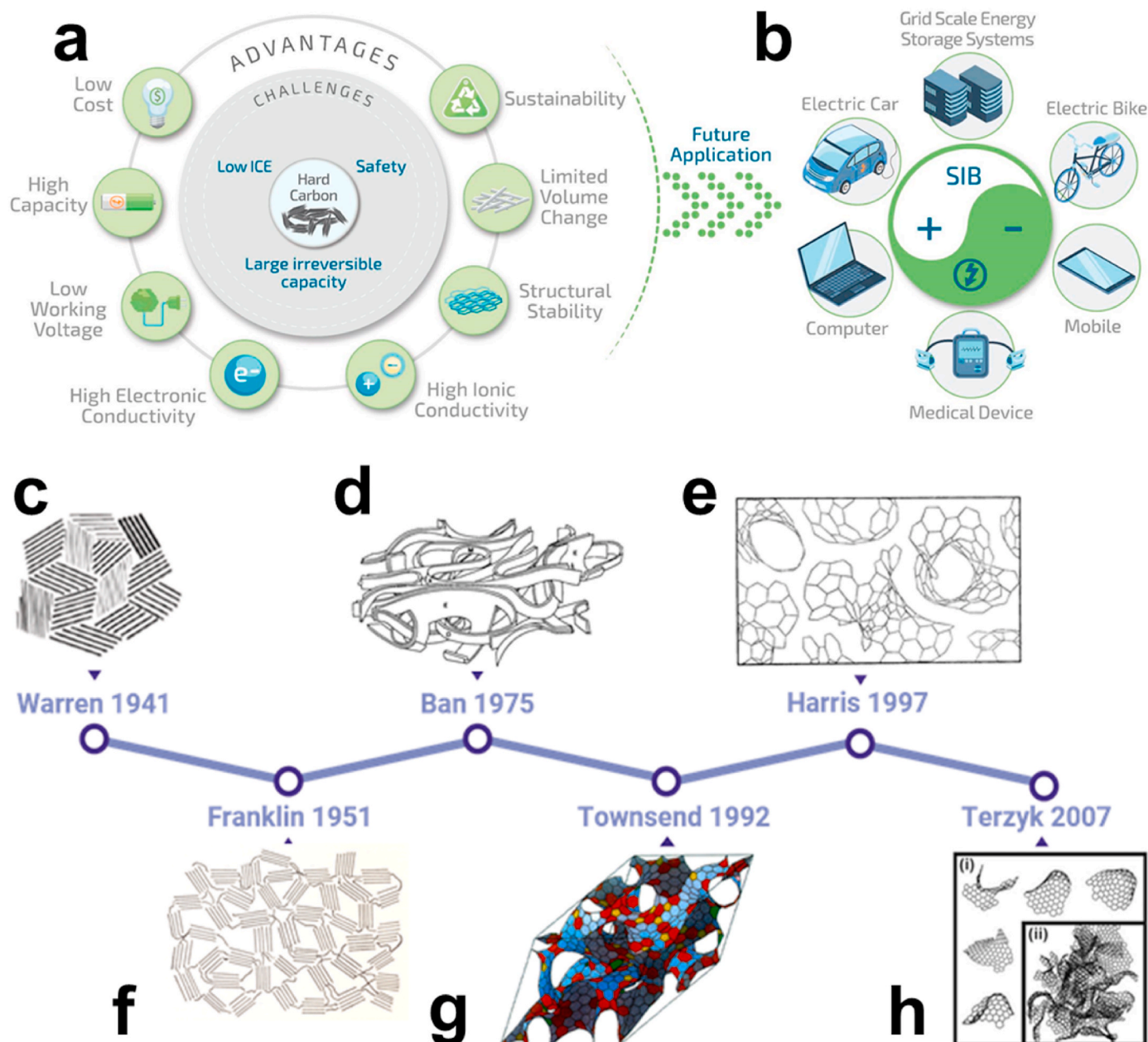


Fig. 1. Representative properties of hard carbons (a) and application of hard carbon anode adopting SIBs (b). Hard carbon models proposed by (c) Warren (1941). Reproduced with permission [45]. Copyright 1934, AIP Publishing. (d) Franklin (1951). Reproduced with permission [46]. Copyright 1951, The Royal Society Publishing. (e) Ban (1975). Reproduced with permission [47]. Copyright 1975, International Union of Crystallography. (f) Townsend (1992). Reproduced with permission [48]. Copyright 1992, American Physical Society. (g) Harris and Tsang (1997). Reproduced with permission [49]. Copyright 1997, Taylor & Francis. (h) Terzyk et al. (2007). Reproduced with permission [50]. Copyright 2007, Royal Society of Chemistry.

2. Models of hard carbon

Since its discovery, several representative models have been proposed with different properties (Fig. 1c–h). In 1941, Warren et al. discovered the first model on the structure of HC that represents randomly oriented graphite nanodomains investigated by the X-ray diffraction (XRD) technique [45]. Later, Franklin et al. suggested another analog version of this model in 1951, wherein the graphite nanodomains are linked by amorphous carbon (sp^3), which prevents graphitization due to cross-linking groups to result in the formation of micropores [46]. This model made it easier to explain the structural properties of HCs; unfortunately, it is difficult to describe the recently reported complex formations using simply a two-dimensional representation of flat sheets. Subsequently, Ban et al. developed a model consisting of a graphite nanoribbons network [47]. To date, this theory is insufficient to explain the impossibility of graphitization since graphene layers have sufficient mobility for graphitization. The models were further improved with the evolution of both advanced characterization methods and computational modeling in the 1990s. In 1992, Townsend et al. proposed a "random schwarzite structure" model using a computational method and claimed that amorphous carbon contains fullerene-like structures [48]. A few years later, Harris and Tsang demonstrated a deeper understanding of the structure of HCs via transmission electron microscopy (TEM) analysis in their work (1997) [49]. In this model, the curvature of graphene is related to fragmented fullerene-like structures, which are aligned to varying degrees, and made of non-graphitized micropores. It is believed that this curvature prevents graphitization. Further, based on previous results from Terzyk et al. a new model consisting of discrete curved carbon layers was

proposed in 2007 [50]. The random scattering of pentagons and heptagons within the curved carbon structure was conducive to stabilizing the curvature from graphitization [50]. Due to the presence of different porosity types, the structure of hard carbon is considered fairly complex. Thus, the widely accepted recent model describing the structure of hard carbon is the "Card-house" or "falling cards" model. In this case, hard carbon is viewed as a mixture of pseudo-graphitic micro-crystallites, amorphous regions, and nanoforms [57].

Among the proposed models, it is evident that the composition of hard carbon (HC) is intricate, featuring disordered carbon structures characterized by numerous defective layers and regions with amorphous characteristics, along with nanopores.

3. Sodium storage mechanism

Due to the amorphous nature of HC, the sodium storage mechanism by change remains still unclear and contradictory [58]. Up to now, numerous sodium storage models have been present, and they can be grouped into three distinct mechanisms: (I) adsorption-insertion mechanism, (II) adsorption-nanopore filling mechanism, and (III) adsorption-insertion and nanopore filling mechanism as shown in Fig. 2.

3.1. Adsorption-insertion mechanism

Seen in Fig. 2a, the capacity obtained in the sloppy high voltage region is mainly due to sodium adsorption in the intrinsic defective areas, edges, and heteroatoms of HC materials. Improvement of sloping capacity is advantageous for rate performance and long-cycle stability, while it is detrimental to the ICE. The low-potential plateau is formed

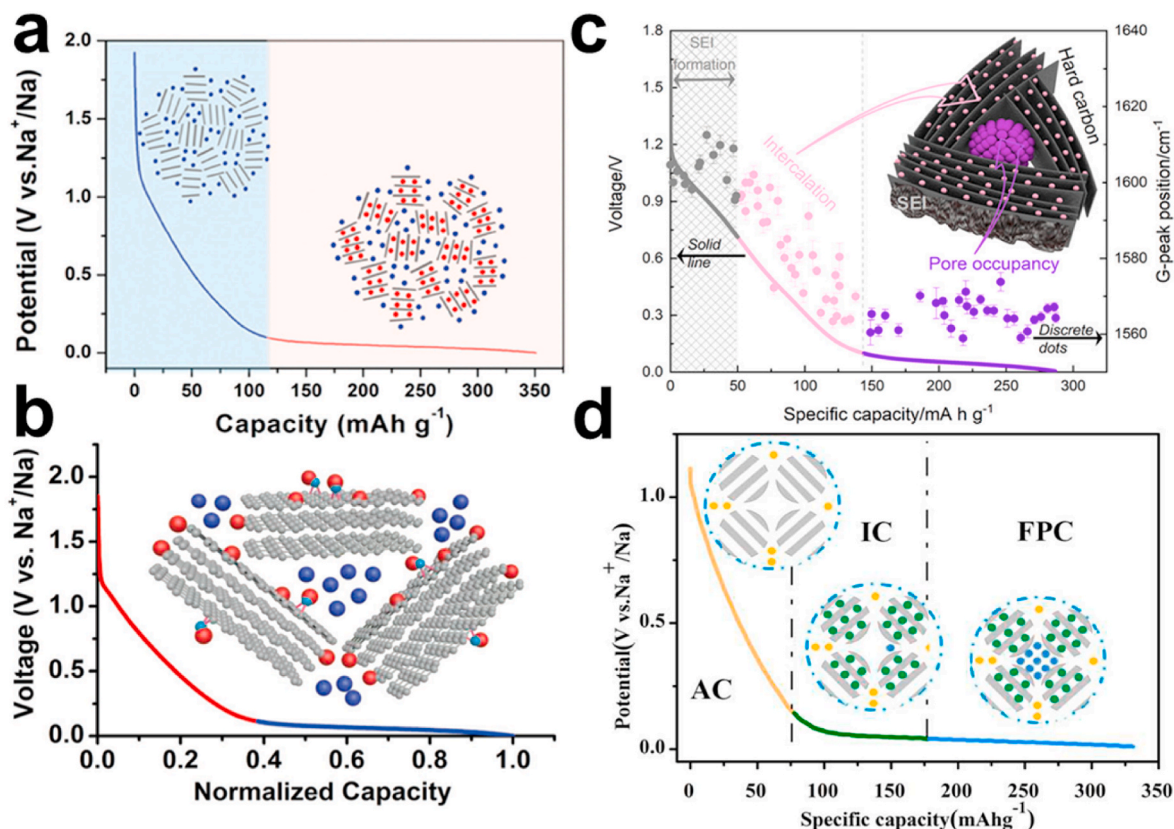


Fig. 2. Three main sodium storage mechanisms in HCs: (a) adsorption-insertion mechanism. Reproduced with permission [59]. Copyright 2017, Wiley. (b) adsorption-nanopore filling mechanism. Reproduced with permission [63]. Copyright 2018, Wiley. (c) adsorption-insertion and nanopore-filling mechanism. Reproduced with permission [64]. Copyright 2020, American Chemical Society. (d) Schematic illustration of the mechanisms for Na-ion storage in hard carbon: adsorption capacity (AC), interlayer intercalation capacity (IC), and filling-pore capacity (FPC). Reproduced with permission [65]. Copyright 2018, American Chemistry Society.

because of the insertion of sodium ions into graphite sheets. According to the theoretical calculation, the optimal d -spacing for introducing sodium ions into a graphitic layer is greater than 0.37 nm.

Qiu et al. investigated the sodium storage mechanism using *in situ* XRD to prove the “adsorption-insertion” mechanism. The microstructure changes during insertion/extraction of sodium ions were observed with *in situ* XRD. The segment I corresponds to the sloping capacity during discharge (sodiation) state, and it illustrates an indistinguishable shift of the peak and fluctuating intensity. Next, the segment II relates to the first section of the plateau capacity, and the peak at 26.6° (2θ) slightly splits, in which there is a negative shift in the diffraction peak while a new peak is formed at 26.2° (2θ). Sodium ion insertion can occur in the graphene sheets at relatively wide distances, resulting in spacing widening and shifting towards the lower angle. At the same time, sodium ion insertion is not possible in graphene sheets with a narrow distance, and the corresponding peak stays at its initial location. During the segment III, the peak located at 26.2° (2θ) minimally changes. By inward diffusion, the expanded graphene sheets can hold more sodium ions without further lattice enlargement. It can be evidenced that the strength of the reflection decreases significantly as the discharge continues, eventually becoming negligible at the end of discharge [59]. Bommier et al. investigated the effect of carbon defects on sodium storage. They observed the effect with increasing carbonization temperature, demonstrating a linear decrease in the carbon defects that can be accompanied by the result of I_D/I_G (integral area ratio of the D-band and G-band in Raman spectroscopy) and reduction in slope capacity. Consequently, the capacity associated with the sloping region was assigned to the carbon defects. Further, the insertion of sodium ion in the plateau area was confirmed by XRD analyses [60]. Ghimbeu et al. evidenced that an increase in carbonization temperature led to a decrease in the functional groups containing oxygen and other heteroatoms, defects, and porosity, which was accompanied by the declined sloping capacity [61]. Additionally, plateau region capacity was increased within the decrease of interlayer distance, which allowed them to consider capacity in the plateau region was linked to the intercalation into graphite sheets [61]. Ding et al. observed that the interlayer spacing was increased from 3.96 Å to 4.16 Å within the voltage range of 0.1–0.2 V. They assigned this observation to the insertion of sodium ions in the plateau region, instead of adsorption in the porous areas. To prove this assumption, they prepared highly porous hard carbon and illustrated that porosity is not proportional to the plateau capacity in low-voltage areas. Furthermore, the reversible shift of the 002 peaks to the lower 2θ was evidenced by *ex situ* XRD analysis. All these studies strengthened the theory of the “adsorption-insertion” mechanism [62].

3.2. Adsorption-nanopore filling mechanism

Even though the “adsorption-insertion” mechanism is supported by a substantial amount of scientific data, several experimental results are insufficient to explain by this mechanism [66]. Cao et al. produced hollow hard carbon with a multi-shelled nanostructure to enlarge the pore volume [67]. The slope capacity did not change as the number of shells rose, showing that the formed micropores were closed. However, the increase of capacity in the plateau region validated the nanopore-filling model [67]. Bai et al. stated that inserting sulfur into the micropores of hard carbon can reduce the plateau at the low voltage region, indicating a connection between the nanopore-filling mechanism and the low voltage plateau [63]. The decreased sloping capacity validated the adsorption mechanism in the sloping region, by the reduced concentration of heteroatoms with defects at higher carbonization temperatures. According to Fig. 2b, sodium ions initially bond to the defect sites or heteroatoms, which have different binding energy, and then they fill the micro/nanopores of the HCs with weak binding energy, similar to the deposition of Na on metal. Lastly, HCs with ether-based and ester-based electrolytes exhibiting similar sodium-insertion characteristics revealed that there were no sodium

ions to be intercalated between the graphene sheets [63]. Li et al. used TEM to analyze the microstructure of hard carbon where the interlayer distance did not expand after discharge to 0 V, which means insertion of sodium ions into hard carbon was negligible [68]. Furthermore, the voids and edges of the HC layer were blurred after sodiation, indicating that these sites were occupied with sodium [68].

3.3. Adsorption-insertion and nanopore filling mechanism

Recent works also propose the mechanism on the three-sodium storage sites: 1) graphene surface containing defects, active sites, and edges, 2) graphene sheets with variable d -interlayer spacing, and 3) nanopores. This mechanism assigns sloping region capacity by the defect/edge surface areas of HCs, which are unrelated to the internal structure. At the same time, the flat plateau region capacity comes from graphene sheets and nanopore filling (Fig. 2c) [64,69,70].

Jin et al. prepared hard carbon material from the resorcinol formaldehyde resin at various pyrolysis temperatures to correlate HC property and sodium ion storage behaviors [65]. Samples carbonized at low temperatures ($<1000^\circ\text{C}$) present microstructure predominated by a large degree of heteroatoms with cross-linking bonds, defected surface areas, and small graphitic layers. At medium temperature ($1000 < T < 1300^\circ\text{C}$), the breakdown of the functional groups led to the significant reduction of the active sites, an increase of stacking graphene layers, and the formation of confined space (closed nanopores). As can be seen from Fig. 2d, the discharge curve can be divided into three intervals considering the variation in diffusivity of sodium ions. First, on the voltage range of 0.1–1.0 V, a large repulsive force is generated because of increased sodium content in the active surface region, and it resists the further adsorption of ions showing a slight decrease in diffusion coefficient (DC). At the same time, this force pushes each sodium ion between graphene layers with suitable d -spacing, hence, the Na-graphite structure has difficulty generating stable compounds which leads to the sudden decrease of DC for Na^+ ions. However, the continuous insertion of the Na^+ ions overcomes a high energy barrier, which results in the Na^+ ions in parallel graphitic layers in the voltage range of 0.1–0.03 V. Lastly, after the low saturation point of voltage, Na^+ ions start to enter the confined area (nanopores) to oppose the energy barrier for electrochemical reaction leading to the rise of the DC [65]. Yamada et al. conducted a comprehensive analysis of the sodiation process by integrating *ex situ* small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) techniques [71]. After sodiation, the WAXS data present shift of 002 Bragg peak toward a low angle, indicating that the interlayer spacing was enlarged. Furthermore, increasing pyrolysis temperature was assumed to enhance the degree of cross-linking of the internal structure, making the sodiation process more difficult. The reduced scattering intensity, as sodiation progressed, can be seen from the WAXS spectra, suggesting that not only sodium ions were filled into the nanopores but also the nanopore filling occurred concurrently with insertion. As a result, their findings suggested that intercalation and pore-filling models correspond to the plateau capacity. However, the contributions of these models vary for the case of different types of HCs [71].

Achieving high performance of biomass-derived hard carbon anode materials for sodium-ion storage requires a comprehensive understanding of the sodium storage mechanism. According to literature survey, the adsorption-intercalation-pore filling model appears to be a suitable representation of sodium storage in HCs. However, the exact charge storage mechanism responsible for a specific voltage range remains uncertain. It is important to note that the pore-filling mechanism pertains to the filling of Na^+ ions into closed pores in HCs, while the charge storage in open pores is classified under the adsorption mechanism. To improve cell performance, it is crucial to validate the exact sodium storage mechanism in the low-voltage plateau region, which has high reversibility and stability against cycling. Therefore, fundamental studies using advanced physical and electrochemical characterization

techniques, in combination with computational methods, are necessary to elucidate the sodium storage mechanism in HCs and advance sodium-based energy storage technology.

Of the three proposed mechanisms for sodium-ion storage, the one involving adsorption-insertion followed by nanopore filling appears to be the most favorable. This conclusion is based on observations from various studies, which have shown that defects have a significant impact on adsorption and capacity during cycling. Furthermore, there was experimental confirmation of d-spacing alterations during discharge within the plateau region. Additionally, it was discovered that closed nanopores have a beneficial impact on capacity. Therefore, in the pursuit of designing practical hard carbon materials based on the adsorption-insertion mechanism, critical considerations emerge to enhance both rate performance and long-cycle stability. The first point involves enhancing surface areas, strategically controlling defects, edges, and introducing heteroatoms. These sites play a crucial role in contributing to the sloping region capacity.

Simultaneously, the design of hard carbon materials should pay close attention to graphene sheets featuring variable d-interlayer spacing. Manipulating the internal structure of the material to accommodate sodium ion insertion within graphitic layers during the plateau region is pivotal. Understanding and fine-tuning the interlayer spacing within the optimal range, as indicated by theoretical calculations, can significantly influence the efficiency of sodium insertion and extraction processes. It can be done by introducing intercalant molecules and high temperature carbonization.

In addition, the presence and characteristics of nanopores within hard carbon materials should be considered in the design process. Strategically creating and controlling nanopores, taking into account factors such as size, distribution, and accessibility, can profoundly impact the accommodation of sodium ions. Tailoring the nanopore structure to provide optimal conditions for sodium ion filling, particularly during low-voltage plateau regions. The creation of a nanopore structure can be accomplished through various methods, including the careful selection of an appropriate precursor, extended carbonization periods leading to increased pore volume, and the application of chemical and physical activation processes.

4. Classification of hard carbons

Since extensive studies of HCs started in the early 2000s, till now a variety of precursor materials, including sugars, like sucrose [72] and glucose [73,74], cellulose [75,75–79], abundant synthetic polymers like phenolic resins, polyaniline (PANI) [80–82], polyacrylonitrile (PAN) [83–85], and biomasses (peels of fruits and etc.) were reported.

These precursors can be divided into three main categories for ease of comparison to synthetic polymers, biopolymers, and biomasses (Fig. 3). Due to the advantages of each category, all three types were investigated in searching for the most suitable precursor for producing HCs.

4.1. Synthetic polymer-derived hard carbon

Synthetic polymers have diverse chemical components with minimal impurities, and most of them are highly miscible in various solvents. Therefore, the key benefit of polymers is the ability to regulate characteristics of HCs by adjusting the synthetic technique through mentioned chemical factors. In addition, the yield of HCs from the pyrolysis of synthetic polymers is relatively high (~40–50 %) in comparison with other bio-precursors. The main shortcomings of the synthetic polymer are toxicity and expensive price compared to other precursors. Recently, widely used polymers for the preparation of HCs are polyacrylonitrile (PAN), phenolic resin, polyvinyl chloride (PVC), and polyvinylpyrrolidone (PVP).

Phenolic resins were investigated to prepare HCs due to the controllable morphology and structure of the precursor [86–88] and was chosen as the most appropriate precursor for large-scale application due

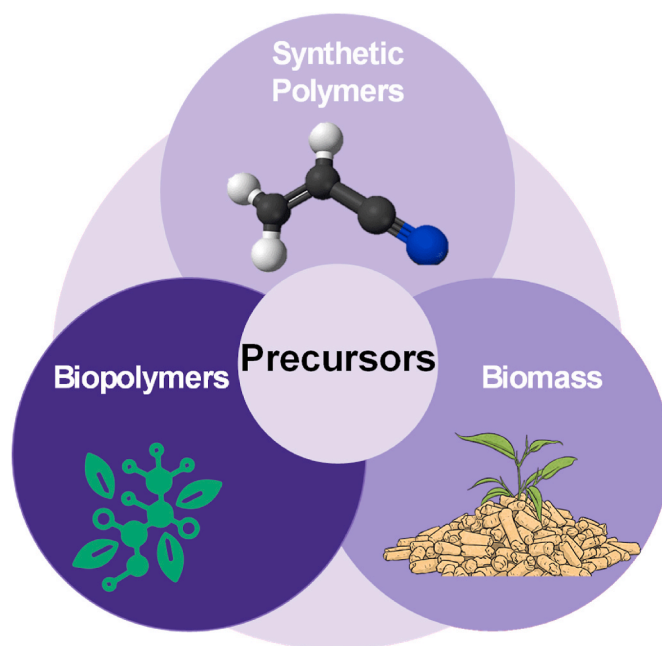


Fig. 3. Hard carbon classification: the main categories of precursors for preparation HCs.

to its high carbon yield (50%), high reversible capacities (Table 1), and desired ICE values. Fabricated nanofibers (CNFs) from low-cost PAN and their compatibility with other copolymers to reach pores structure as well studied (Fig. 4a) [89,90]. The advancement in electrochemical performance of those materials was ascribed to their interconnected frameworks to reduce contact resistance, and highly porous channels were responsible for shortening the transfer distance for electrons and Na^+ ions (Fig. 4b) [90]. Bai et al. reported HCs from PVC nanofiber precursor (Fig. 4d) and the improvement was attributed to the uniformly distributed small particle size, since it assisted in obtaining a greater contact area between the electrode and electrolyte to shorten the diffusion path for Na^+ ions [91]. Additionally, same authors contributed to the fabrication of mille-feuille-shaped HC material from the PVP (Fig. 4c). As consequence, it was advantageous for the shortening of diffusion distance, which affected low impedance and fast Na^+ diffusion [92].

The versatility of synthetic polymers positions them as highly promising candidates for generating hard carbon. Nevertheless, the utilization of harmful organic solvents is discouraged when aiming for large-scale production because of their toxicity. Aside from that, a substantial portion of the capacity is derived from the sloping region, leading to a higher operating voltage which negatively affects the overall energy density of the full cell.

4.2. Biopolymer-derived hard carbon

Another category is biopolymers, which are sustainable, biodegradable, and low-cost that can be generated from renewable raw materials such as plants (e.g., corn, sugarcane, potatoes), microorganisms (e.g., bacteria or yeast), and occasionally even animal-derived materials (e.g., collagen) [94,95]. The average yield of carbon is comparable to that of biomass, which is lower than 20 %. Plants are the most abundant and cost-effective source of polysaccharides (sucrose, cellulose, and D – glucose). Chitosan, lignin, and chitin are examples of polysaccharides derived from animal and microbial sources used as a precursor for the synthesis of HCs [96,97].

Sucrose is a type of complex carbohydrate that is commonly utilized in the production of high-capacity materials for sodium-ion batteries (SIBs). In 2000, Steven and Dahn reported sucrose-derived HC, one of

Table 1

Classification of precursors for battery-grade HCs used for SIBs.

Classification	Precursors	Capacity [mAh g ⁻¹]	ICE [%]	Voltage range [V]	References
Synthetic Polymer-derived	polyacrylonitrile	266	80	0.001–2	[90]
	phenolic resin	284	88	0.01–2	[132]
	polyvinyl chloride	271	70	0.01–2.5	[92]
	polyvinylpyrrolidone	271	–	0.01–2.5	[91]
Biopolymer-derived	sucrose	300	–	0–2	[89]
	cellulose	310	84	0.05–3	[72]
	D-glucose	330	–	0.1–0.5	[73]
	waste of shrimp skin	434.6	–	0.001–3	[116]
Animal biomass	cuttlebone	640	51.5	0–3	[115]
	bacterial cellulose	276	50	0.1–2.5	[56]
Microbial biomass Plant biomass	Maple tree	332	–	0–2.5	[120]
	Coconut	314	–	0.01–3	[121]
	Dandelion	364.3	–	0.001–3 0.01–	[123]
	Kelp	205	–	2	[124]
	Cotton	315	83	0–2	[68]
	Date palm	300	88.4	0.02–2	[119]
	Typha	204.8	–	0.01–3	[125]
	Switchgrass	225	64	0.01–2	[126]
	Marple leaf	360	74.8	0–2.5	[127]
	Outmeal	272.4	46.68	0.001–3	[128]
	Corn cob	298	6	0.01–2	[129]
	Garlic	260	50.7	0.01–3	[117]
	Spinex	386	–	0.05–3	[122]

the first for SIBs studies [98]. Later Kubota et al. focused on same precursor modifying the average stacked carbon interlayer distance, as well as the number of stacking layers, layered domains, and interstitial voids (Fig. 4e and f).

Afterwards, polysaccharides have been widely employed in the synthesis of high-capacity (HC) materials to enhance their capacity, internal combustion engine (ICE) performance, and cyclability. Bomnier et al. attempted to predict the capacity of HCs synthesized from sucrose depending on the porosity with additionally, activation with CO₂ to increase capacity [99]. Following that, doping with graphene oxide investigated to prevented caramelization, which simultaneously improved the electrode performance due to the low porosity assisted by the graphene oxides (Fig. 4g) [93]. A recently updated reports included the results of HCs from cellulose [100], D – glucose [73].

The introduced synthesis of HCs with different precursors seems to diverse the electrode performance of HCs due to the complicated compositions of the used precursors, regardless of the high carbon residue rate and low cost of the biopolymer precursor. The reaction mechanism of cross-linking oxidation process is still an issue that has to be resolved. To fully optimize the properties and functionality of the resulting biopolymer-derived HCs, the pre-oxidation and carbonization processes must be precisely modulated.

4.3. Biomass-derived hard carbon

Biomass is a group of sustainable, abundant, and low-cost fuels that contains carbon and some heteroatoms like oxygen, sulfur, nitrogen, and phosphor [52,101]. These are interesting candidates as precursors for producing high-performance HC anode materials due to the environmental friendliness of those biomass materials [102]. A survey in 2003 presents that ~730 Tg (1 Tg = 10¹² g) of biomass is burned in one year, for example, crop residues burning in the fields contributing about 34% in total [103]. Open-air burning of bio-waste produces CO₂ and other local pollutants such as volatile organic compounds (VOCs) and sulfur dioxide, all of which lead to the high concentration of smog observed in many Asian and South American countries [104]. As a result, there is widespread agreement on recycling and reusing bio-waste. Furthermore, biomass waste can be considered a reliable large-scale carbon source due to the active "industrialization" of agriculture, which results in massive amounts of well-defined biomass and food waste as a response to an ever-growing world population and improving living standards [105]. Transforming bio-waste into battery-grade electrode

materials is much more attractive regarding the utilization of limited resources, given the current demand for mobile devices and the future demand for electric vehicles (EVs). Therefore, battery-grade electrode materials developed from biomass provide attractive opportunities. Successful bio-waste-derived electrode materials would be environmentally friendly and potentially highly profitable by valorizing otherwise unused waste.

Following previous studies, HC electrodes derived from various biomasses exhibited specific capacities ranging from 100 to 350 mAh g⁻¹ at low current densities [106]. In this case, biomasses may present an ideal carbon source compared with commercial precursors such as some polymers [107]. Simple direct carbonization [68,108], hydrothermal carbonization [109,110], and physical or chemical activation [98,99] are used to convert biomass into HCs. During the pyrolysis process, various gases (CO, CH₄, H₂, and H₂O) are usually emitted. The residual mass is transformed into amorphous carbons following substantial cross-linking and aromatic ordering [111–113]. In general, the preparation process of HCs from biomass can be divided into: a) washing the biomass with water, b) drying, c) activation, and d) thermal treatment at high temperatures between 600 and 1600 °C in an inert atmosphere [114].

Biomass-derived carbon anode materials are intensively investigated in SIBs and can be classified according to precursors: 1) animal biomass (Fig. 5a and b) [115,116], 2) microbial biomass (Fig. 5c) [56] and 3) plant biomass (Fig. 5d) [117,119–131]. It has been found that the use of microbial biomass as a precursor is a complex and long-term process, since it must be cultivated artificially. Essentially, animal biomass (such as bone, shell, and skin) expanded as highly mesoporous carbons, which were subsequently demonstrated to be effective sodium storage materials. In this sense, these natural composites themselves are composed of heteroatom-rich components with nanosized hard templates with the exquisitely pre-organized structure. Leaning on this, structural fact of hetero atom-rich mesoporous carbons demonstrated outstanding sodium storage performances with superior reversible capacities (Table 1) [115,116], but they are more susceptible to metamorphism and long-term preservation. As a result, microbial and animal biomasses are excluded from the list of candidates for commercial HC production. In case that we consider plant biomasses; they have a wide range of sources and are relatively easy to store and synthesize. Consequently, plant-derived carbon materials have received much attention and are widely investigated.

HCs from different precursors have variable electrochemical

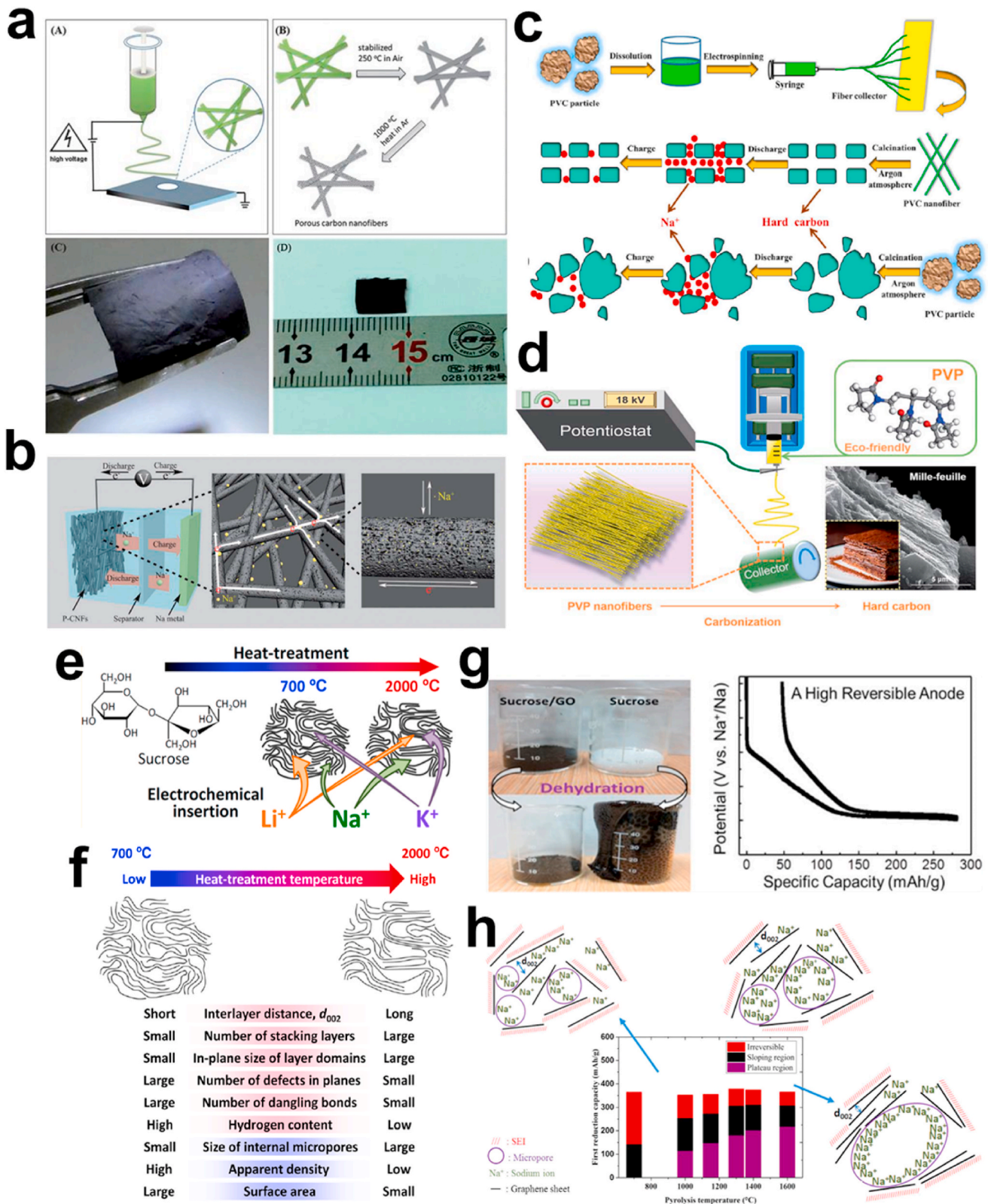


Fig. 4. (a) Schematic illustration of the synthesis process for flexible electrode derived from PAN. (b) Schematic illustration of sodium storage mechanism in P-CNFs. Reproduced with permission [90]. Copyright 2014, Royal Society of Chemistry. (c) Schematic diagram of synthesis routes and Na⁺ storage behaviors of hard carbon. Reproduced with permission [92]. Copyright 2015, American Chemical Society. (d) Schematic illustration of the synthesis process for the mille-feuille shaped hard carbons derived from PVP. Reproduced with permission [91]. Copyright 2017, Royal Society of Chemistry. (e) Sucrose-derived HC at different heat treatment temperatures (HTTs) in the range of 700–2000 °C. (f) Schematic illustrations of structures of the hard carbon samples prepared at 700 °C and 2000 °C and the structural parameters. Reproduced with permission [72]. Copyright 2020, American Chemical Society. (g) Low surface-area hard carbon derived from sucrose with GO doping. Reproduced with permission [93]. Copyright 2015, American Chemical Society. (h) Description of pyrolysis temperature impact on the structure and electrochemical performances of hard carbons. Reproduced with permission [75]. Copyright 2016, Elsevier.

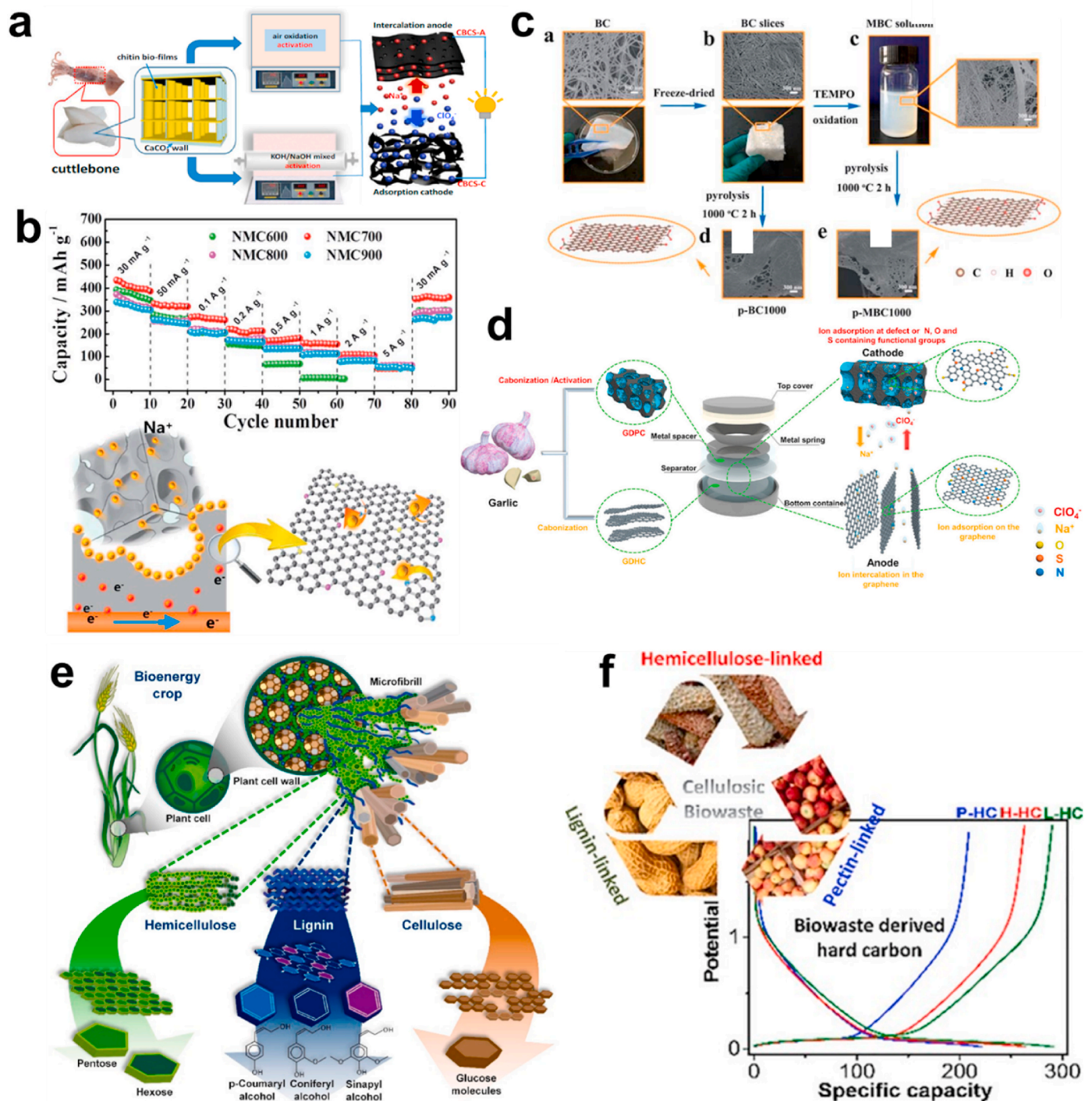


Fig. 5. (a) Schematic illustration of the material synthesis process and the relevant anode–cathode charge-storage mechanisms in SIBs. Reproduced with permission [115]. Copyright 2018, American Chemical Society. (b) Rate performance of the NMCs as anode for SIBs and Schematic illustration of sodium storage mechanism in NMCs. Reproduced with permission [116]. Copyright 2017, Royal Society of Chemistry. (c) Fabrication process of HC from bacterial cellulose. Reproduced with permission [56]. Copyright 2017, Royal Society of Chemistry. (d) Illustration of the Preparation Process of the HC from garlic waste and the Mechanisms for the Na-ion Storage. Reproduced with permission [117]. Copyright 2019, American Chemistry Society. (e) Structure of lignocellulosic biomass and its biopolymers; cellulose, hemicellulose, and lignin. Reproduced with permission [97]. Copyright 2019, MDPI. (f) Schematic illustration of biomass-derived HCs for SIBs. Reproduced with permission [118]. Copyright 2017, Wiley.

characteristics due to the difference in the chemical composition of each biomass source (Table 1). In general, the structure of plant-derived biomass precursors is extremely different, containing a range of biopolymers as illustrated in Fig. 5e. Cellulose is the most abundant component of plant-derived biomass. Therefore, cellulose-based

biomass can be classified into three subclasses: pectin-, hemicellulose- and lignin-based materials (Fig. 5f) [118]. It is known that lignin and hemicellulose-type materials are highly cross-linked and non-crystalline, making them non-graphitizable. When lignin is pyrolyzed, it usually results in the conversion of biomass into porous carbons,

particularly in presence of the lignin that contains impurities. Thus, different biomass will produce carbon materials with various structural features. For instance, shaddock peel, which is a plentiful and natural carbon precursor, comprises approximately 78% hemicelluloses, 7–21% pectin, and some sugars [133]. Another example, is pectin content in the banana peel can reach up to 20%, and 35% can be free sugars [134]. Additionally, the structure of nutshells is composed of lignin content ranging between 30 and 40 %, 25 % of cellulose, and 30% of hemicellulose [135]. It is also worth noting that the lignocellulose composition of peanut shells varies significantly between the inner and outer layers [136]. Among biomass, fruits have a higher amount of pectin than other materials including leaves and nutshells [137]. Furthermore, differences in lignocellulosic composition can cause untenable physical, chemical, and electrochemical properties of biomass-derived HCs for sodium storage [135].

Dou et al. [118] reported a comparative study on HCs belonging to three different classes: corncocks (hemicellulose-based), apples (pectin-based), and peanut shell (lignin-based), and tried to explain the impact of the biomass structure relating to the electrochemical properties. The material generated from peanut shells (L-HC) had the highest specific capacity (298 mAh g^{-1}) with 98% capacity retention for 300 cycles at 0.1C. Plant biomass materials with their well-balanced proportions of lignin and pectin appear to be the ideal HCs for SIBs. One prevents the crystallization of equilibrium graphite, and the other allows partial ordering of the graphene layers [136].

In addition, this type of precursors rather than more other carbon sources naturally have unique secondary microstructures. The essential morphology and porosity of bio-wastes have the potential to rapid ion diffusion, improve electrolyte percolation as well as ionic and electronic conductivity [138]. Zhang et al. investigated this characteristic with lotus stem precursor which itself has inherently organized hierarchically of channels, resulting in the formation of a regulated three-dimensional structure subsequent to pyrolysis [139]. Lotus stem hard carbon delivered 351 mAh g^{-1} reversible capacity with 70% ICE value at a current density of 40 mA g^{-1} . Simultaneously, some researchers noticed that pollen granules manifest an iconic morphology consisting of hollow spheres. In their study, pollen grains were available to reveal the porous carbon interconnected matrix and thereby improve electron conductivity, ion diffusion and sodium-ion storage capability. The interconnected structure remained intact and undamaged during the hydrothermal treatment process. Based on the findings of electrochemistry, we are able to observe the impact of such a structure. The samples that demonstrated the maximum performance in terms of reversible capacity were those that exhibited a capacity of 135 mAh g^{-1} at 100 mA g^{-1} [138,140]. Because of hundreds of millions of years of progressive evolution, biomass has developed a hierarchical porosity structure that may enable effective circulation and exchange for metabolism in nature. In addition, a chemical composition allows different porous structures to make as unique. These advantages emphasize the importance of biomass as raw materials for high-performance HC anodes, which has drawn significant attention for future research direction. Due to various types of precursors and varying preparation conditions, the electrochemical performances of HC anodes derived from biomass vary greatly. However, this benefit is due to the presence of cellulose and hemicellulose of which these are common subunits for carbonization to HCs that we have highlighted in this chapter.

5. Preparation conditions for the bio-waste derived hard carbon

In this chapter, we focused on HC materials derived from plant biomass waste according to the pyrolysis temperature to describe the corresponding characteristics, electrochemical performance, and associated mechanism. More interestingly, the HC materials synthesized from different plant biomass precursors have varied in microstructures after carbonization. There are also significant differences in sodium storage capabilities. Accordingly, the selection of the initial source of the

precursor is of utmost significance for carbonization temperature. The general composition (hemicellulose, pectin and lignin-based) of the bio-waste precursor, the quantity of contaminants, and the requirement for pre-treatment, activation steps are all significant factors to keep into consideration when selecting initial biomass precursor. Consider the case of cellulose-based raw material, its regular structure, substantial amount of carbon and affordability from a wide variety of plant sources make it commonly initial material for HCs. Lignin-based material aids in producing HC with preferable electrochemical characteristics due to its complicated aromatic structure. Similarly to cellulose-based, it is an essential component of plant cell and hemicellulose-based materials found as a contributor for amount of carbon in HCs. Furthermore, important fact in order to adjust the properties of the hard carbon that is produced, it is possible to improve its performance by selecting right raw material. Giving that, precursors must meet the unique demands of sodium-ion batteries in terms of to hold sodium ions during de/intercalation. Then through careful investigation of initial potential precursors and carbonization temperature some novel and practically applicable HCs can be realized.

5.1. Low-temperature carbonized HC ($< 1000^\circ\text{C}$)

Low-carbonization temperature is mainly utilized for the synthesis of heteroatom-doped or activated HC materials. The reason why doping is conducted at low temperatures ($600\text{--}900^\circ\text{C}$) is to retain heteroatoms in the structure. For carbonizing temperatures above 900°C , the C–N and C–S bonds will break down rapidly [141]. Likewise, the C–P, –P–O, –P=O configurations are formed approximately at 700°C when oxygen atoms initiate to bond with the phosphorus. At the same time, the atoms start to interact with aromatic rings. Nevertheless, the –P=O is eliminated by increasing the reaction temperature (at 800°C), resulting in decreased doping level. In general, HCs carbonized at low temperatures have disordered structure, large interlayer distance, low degree of graphitization, and increased heteroatoms content. Table 2 compares the physical properties of HCs produced from orange peel, pomelo peel, and pinecone at the carbonization temperature ranging from 700 to 900°C .

Xiang et al. used orange peels as a precursor and activated it with KOH to synthesize non-graphitized HC at 800°C . The authors claimed that a porous and disordered structure was obtained after the activation with KOH. This type of structure may accelerate facile penetration of electrolytes so as to endorse space for sodium storage [142]. Another work done by Hong et al. demonstrated pyrolyzing of pomelo peel precursors at 700°C activated by H_3PO_4 . The synthesized HC had a 3D-connected porous structure with a large number of nanopores. This porous structure contributes to charge transfer reactions, ameliorating the interfacial contact between electrode and electrolyte and shortening the diffusion path of sodium ions [143].

5.1.1. Effect of low-temperature carbonization on physical properties

According to the investigation by Gomez-Martin et al. low-temperature samples ($800\text{--}1000^\circ\text{C}$) show ultra-microporous characteristics [144]. They found that HC samples carbonized at 800°C exhibited open pores ranging from 2 to 3 nm as confirmed by N_2 physical adsorption measurements with the two-dimensional non-local density functional theory (2D-NLDFT). Further elevation of temperature from 800°C led to increasing in open pores size greater than 4 nm [144]. Similar findings were discovered by Kubota et al. the average size of micropores was increased from 0.65 nm to 0.85 nm by increasing pyrolysis temperature from 700 to 1000°C using a fitted SAXS pattern [132]. This trend was also observed for HCs prepared from phenol resin [145], and cellulose [76]. Additionally, the HC sample carbonized at a low temperature (800°C) had a higher density in comparison with the sample carbonized at a higher temperature (1200°C). The high skeletal density means that the volume of the closed pore is low at 800°C [144].

At low carbonization temperatures, the surface of HC mainly contains extrinsic defects with increased heteroatom content, and this

Table 2

Physical properties of HCs pyrolyzed at low temperatures.

Precursor	Pyrolysis temperature	SBET [$\text{m}^2 \text{g}^{-1}$]	I_D/I_G	d_{002} [nm]	L_a [nm]	L_c [nm]	References
Orange peel	800	638	2.56	–	–	–	[142]
Pomelo peel	700	1272	–	–	–	–	[143]
Pinecone	800	557	3.03	0.417	9.59	1.25	[130]
Pinecone	850	400	3.03	0.413	10.52	1.43	[130]
Pinecone	900	395	2.94	0.407	10.70	1.46	[130]

content is changed in response to the increase in the pyrolysis temperature. Chen et al. observed that the relative C-O content was high in samples carbonized at 700–900 °C, and it corresponded to 77.07% and 58.57%, respectively [146]. Generally, C-O is located at defect areas and is usually transformed to C=O content at higher carbonization temperatures. Additionally, according to Miao et al. rising carbonization temperature from 600 to 900 °C decreased pyrrolic nitrogen percentages from 3.94 to 1.15% and increased the pyridinic content of the nitrogen from 1.75 to 2.07%, which was led by the self-arrangement of C-N bonds [146]. Regarding intrinsic defects, low pyrolysis temperature (<1000 °C) is insufficient to decrease the concentration of intrinsic edge defects. Moreover, the intrinsic defect is proportional to the graphitic ordering of HC, which means that a highly disordered structure is dominant in samples carbonized at low temperatures. Gomez-Martin et al. employed Raman spectroscopy to compare the defect concentration by calculating the I_D/I_G value with increasing the heat-treatment temperature [144]. Hou et al. synthesized HCs from waste cigarette butts at 700–800 °C and prepared HC had interlayer distances of 0.387 nm and 0.383 nm, respectively [147].

The above works indicate that HCs carbonized at low temperature have larger curvature with increased interlayer distance due to the presence of heteroatoms and defects as mentioned before. Such a large interlayer distance is favorable for sodium storage.

5.1.2. Effect of low-temperature carbonization on electrochemical performance

HCs produced below 1000 °C usually deliver a low initial reversible capacity (200 mAh g^{-1}). There are a lot of defective area and surfaces for the HCs synthesized at low temperature as mentioned above; therefore, the HC electrodes usually have low ICEs, for which a large amount of sodium are consumed to form solid-electrolytic interphase (SEI) layers, at the first cycle associated with the large surface area.

Xiang et al. synthesized HC from orange peel using the activation with KOH. The initial capacity of the hard carbon anodes delivered 497 mAh g^{-1} at 0.5 A g^{-1} during the first sodiation, while the desodiation resulted in a small capacity of 156 mAh g^{-1} that was retained for 3000 cycles [142]. The low carbonization temperature preserves the oxygen content in HCs, and the functional groups containing oxygen could increase the electrochemical properties in the slope region [148]. The cycling performance of the H_3PO_4 -activated HC electrode showed 200 mAh g^{-1} , while natural pomelo peel without acid treatment delivered only 110 mAh g^{-1} [143]. Zhang et al. analyzed cyclic voltammetry of HC prepared from pinecones at different temperature ranges. The HC carbonized at 500–800 °C exhibited no sharp specific redox reaction in CV data. By contrast, samples carbonized above 850 °C present sharp distinct reduction and oxidation peaks in the voltage range of 0.001–0.25 V, which indicates insertion/extraction of sodium ions into the HC. Additionally, the sharp redox curve for HC carbonized at 850 °C indicates a higher coulombic efficiency and reversible capacity [130].

Low-temperature carbonization is a process that can enhance the heteroatom content and interlayer distance in HC materials by preserving the heteroatoms within the structure. This process, however, leads to a reduction in the degree of graphitization, resulting in a disordered structure with a larger interlayer distance (See Table 2) and increased heteroatom content. These characteristics provide HC materials with a larger curvature that is highly beneficial for sodium storage, despite

their low initial reversible capacity due to a large surface area (Table 2) and defective surfaces. Various research studies have emphasized the significance of porous and disordered structure of HCs in promoting charge transfer reactions, shortening the diffusion path of sodium ions, and improving the interfacial contact between the electrode and electrolyte.

5.2. Medium temperature carbonized HC (1000–1300 °C)

Most biomass precursors are pyrolyzed at a temperature range of 1000 °C or above to obtain HCs with the formation and growth of carbon layers in planar hexagonal networks [102]. This structure is characterized by amorphous regions including the graphitic structure and consists of aligned layers of sp^2 (graphene) in small dimensions [88]. As can be seen from Table 3, at higher temperatures, the specific surface area decreases significantly in comparison with low-temperature carbonization as a result of the pore blocking caused by the secondary reaction products of the tar, which produces closed pores [149].

Dou et al. studied the effects of the biomass sources on the structural and electrochemical properties of HCs using different categories of precursors like peanut shell, apple waste, and corn cobs carbonized at 1100 °C [150]. The study compared the chemical composition of different classes like lignin-based, pectin-based, and hemicellulose-based precursors. The result showed that the composition and structure of biowastes have a decisive influence on the final structure, surface area, and elemental composition of HC. Among the studied materials, HC from peanut shells (L-HC) showed the best specific capacity and good cycling stability due to the structural stability of lignin-based materials.

HC derived from banana peel synthesized at 1100 °C was studied as an anode material SIBs [134]. The observed pseudo-graphite showed good properties ascribed to the three distinct characteristics: (a) dilated intergraphene spacing for Na^+ intercalation at low voltages; (b) highly accessible near-surface nanopores for Na metal filling at low voltages, and (c) actual defect content in the graphene planes for Na^+ adsorption at higher voltages.

5.2.1. Effect of medium temperature carbonization on HC properties

Carbonization at temperatures ranging from 1000 °C to 1300 °C results in a porous structure with flake-like and honeycomb-like features. Aerie et al. studied HC from Rambutan peel, which has flake-like morphology with agglomerated carbon spheres after carbonization [151]. With increasing the temperature, the cross-linking of carbon spheres became faster, and pore volume was significantly changed. This flake-like morphology can help to improve sodium ion and electron transfer. In the case of honeycomb morphology, the low specific surface area was observed due to small pore size and improvement of crystallization degree of the microcrystallites. Decreasing open pore volume by increasing carbonization temperature is observed in this type of morphology [151]. In the work of Qin and his colleagues, the average thickness of a graphitic microcrystallite layer along the c -axis (L_c) was 1.07 nm for HC synthesized at 1200 °C [155]. The same tendency was observed for hard carbons from cherry petals at 1000 °C, corresponding to 1.13 nm. According to previous studies, the average thickness tends to increase at medium temperatures, which means that many graphite domains have formed. Concisely, the average number of graphitic layers

Table 3

Physical properties of HCs pyrolyzed at medium temperatures.

Precursor	Pyrolysis temperature	SBET [$\text{m}^2 \text{g}^{-1}$]	I_D/I_G	d_{002} [nm]	L_a [nm]	L_c [nm]	References
Rambutan peel	1000	282	0.85	0.388	–	–	[151]
Cherry petal	1000	1.86	1.02	0.44	2.62	1.13	[152]
Apricot shell	1000	12.5	0.64	0.372	5.16	1.24	[153]
Banana peel	1100	19.3	0.91	0.391	4.15	1.59	[134]
Reed straw	1300	36.20	0.66	0.391	4.52	1.60	[154]
Corn stalk	1300	165.4	0.98	0.372	0.71	1.07	[155]

and the L_c were increased but the d_{002} value was decreased from the obtained HC [152].

The chemical composition at medium temperatures implied an increase in carbon content with increasing pyrolysis temperature. Sun et al. reported that the carbon content gradually increased from 91.08% at 800 °C to 97.53% at 1200 °C, while the oxygen content decreases from 6.32% to 2.47% [133]. Increased contents of hydrogen and nitrogen ingredients were observed in the work of Zhu et al., where they used the apricot shell as a precursor and a new reductive method of pyrolysis [153].

According to earlier studies, increasing hydrogen content induces better absorption of sodium ions, whereas increasing nitrogen content assists in improvement in electrical conductivity and electrode performance. It means that H_2 reduction accompanies the formation of some defects like covalent and dangling bonds that are involved in the enhancement of the ICE.

5.2.2. Effect of medium temperature carbonization on HC electrochemical performances

The carbonization temperature was shown to substantially affect the electrochemical properties of hard carbon as an anode material. An increase in the pyrolysis temperature affects the L_c value and the number of layers. In addition, it reduces the interlayer distance, pore size, and defect sites, thus affecting the electrochemical characteristics (Fig. 6a and b). From the literature review, it was found that increasing the carbonization temperature leads to a decrease in specific capacity on the slope area whereas the capacity increases in the plateau region. The two models of the mechanism were proposed in the work of Wang et al. [154] HCs from reed straw precursors were carbonized at 1300 °C, which exhibited a high reversible capacity of 372 mAh g^{-1} with a good ICE of 77.03%. The mechanism was explained as electrodes can store more sodium ions. The capacity decreased on the slope region due to defect sites and adsorption in micropores, while more capacity was

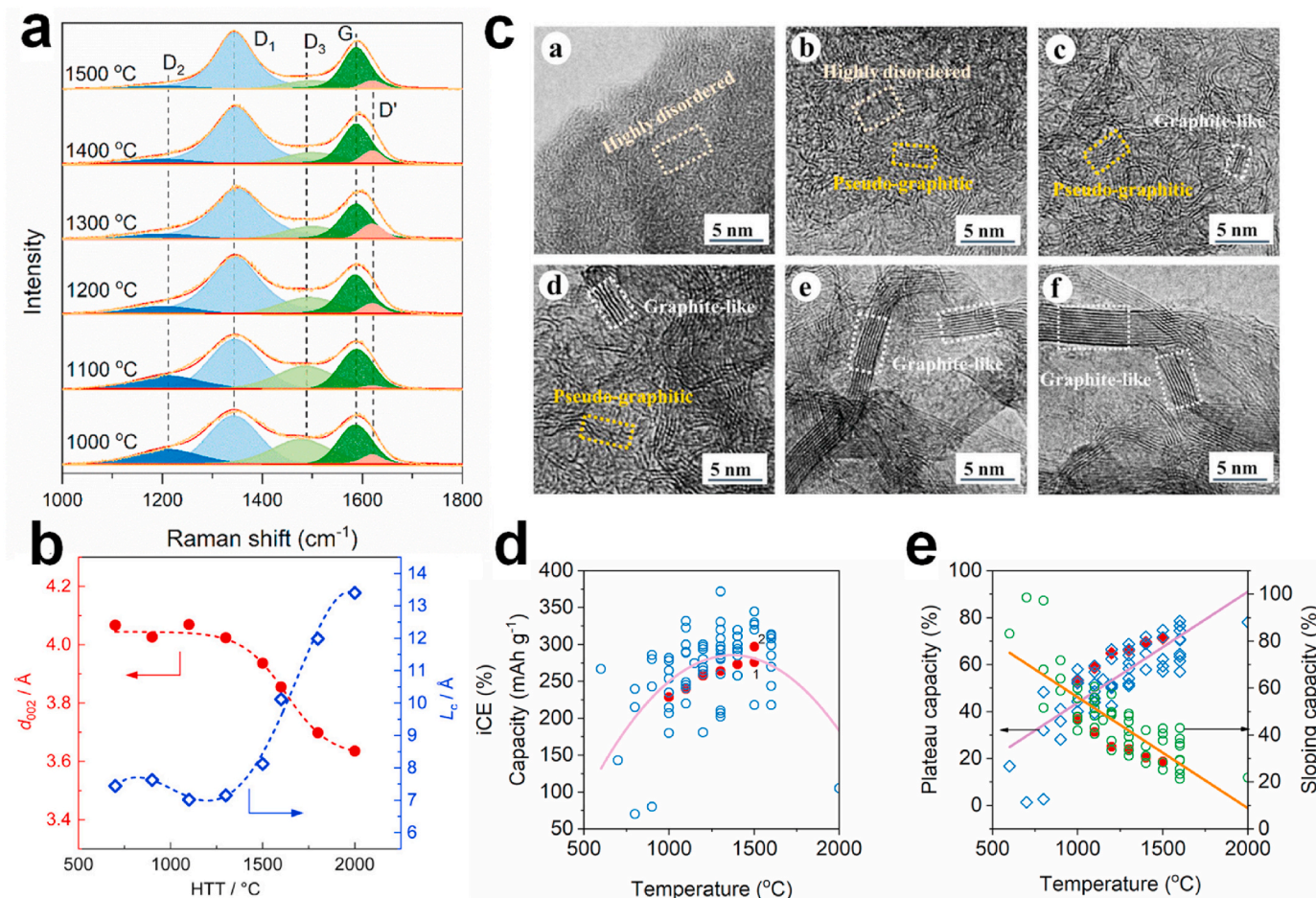


Fig. 6. Material characteristics and electrochemical performance of HC at different carbonization temperatures: (a) Peak deconvolution of the Raman spectra. Reproduced with permission [94]. Copyright 2022, Elsevier. (b) Interlayer distances of carbon layers and crystallite sizes. Reproduced with permission [72]. Copyright 2020, American Chemical Society. © HRTEM images of HC pyrolyzed at 600–2500 °C. Reproduced with permission [157]. Copyright 2019, Wiley. (d) Reversible capacity and e Capacity contributions from the sloping and plateau capacities. Reproduced with permission [94]. Copyright 2022, Elsevier.

delivered on the plateau region through the insertion of sodium ions in graphitic layers [154]. Anode material prepared from cherry petals exhibited outstanding electrochemical performance with a capacity of 300.2 mAh g^{-1} at 20 mA g^{-1} . According to electrochemical studies, the authors proposed the sodium storage mechanism: i) the high potential slope region is related to the absorption of sodium on the surface; ii) the low slope region is based on the intercalation of sodium ions into graphite sheets [152]. The same sodium storage mechanism was reported in the study of Zhu and his colleagues where prepared HC material from sorghum stalk and optimized pyrolyzed temperature (1300°C) to deliver the best cycling performance (245 mAh g^{-1} after 50 cycles) through a charge transfer reaction of an “adsorption-insertion” mechanism [156]. The nature of the corn stalk is hollow tubular with an open pore structure in comparison with cherry petals and it allows easier transport of sodium ions and electrolyte diffusion/penetration. Consequently, the HC showed a stable reversible capacity of 231 mAh g^{-1} after 200 cycles at 0.25C [155]. Surprisingly, shaddock peel-derived HC material synthesized at 1200°C demonstrated a very high reversible sodium storage capacity, 430 mAh g^{-1} at 30 mA g^{-1} [133].

At medium-temperature carbonization, the structure of HC is composed of amorphous regions with graphitic structure and small, aligned layers of sp^2 . At temperatures between 1000°C and 1300°C , HC develops a porous structure with flake-like and honeycomb-like features. The increase in carbonization temperature leads to a decrease in specific capacity on the slope area, while the capacity increases on the plateau region. This is because the increase in temperature results in a reduction of the interlayer distance (See Table 3), pore size, and defect sites, which impact the electrochemical characteristics of HC. HCs obtained from medium temperature carbonization exhibit excellent specific capacity and cycling stability due to their structural stability.

5.3. High temperature carbonized HC ($>1300^\circ\text{C}$)

At the high carbonization temperature, structures that are more ordered and an increase in the turbostratic agglomeration of carbons are observed. The lowest surface area and pore volume values are obtained at high carbonization temperatures because of the ordering, and an increased number of formed graphene planes. The graphitization degree of the hard carbon structure improves with an increase in annealing temperature due to the elimination of surface functional groups, defect concentration, and porosity. The physical properties of hard carbon derived from four different precursors at carbonization temperatures 1400 – 1600°C are shown in Table 4.

5.3.1. Effect of high-temperature carbonization on HC properties

The ordered structure of hard carbon was reported by Wang et al. where HC was synthesized from natural rice husk pyrolyzed at a temperature between 900°C and 1600°C [158]. They observed aggregation of turbostratic carbon as the carbonization temperature rises. The disordered structure of mesoporosity enhances electrolyte transport, hence, shortening the diffusion distance for Na^+ . They also pointed out that interlayer spacing moderately changes to lower values with increasing carbonization temperature up to 1600°C (Fig. 6c). Zhang et al. investigated lotus stem precursors, carbonized at 1200°C , 1400°C , and 1600°C . The pore size distribution becomes increasingly concentrated at 2 – 4 nm as the temperature rose from 1200 to 1400°C , while the open pore volume decreased with increasing the treatment

temperature [139]. As a result, heteroatoms were eliminated and the local structural ordering was enhanced [139]. During carbonization at high temperatures, the content of carbon increases because more heteroatom functional groups are removed from the surface. The same tendency of the carbonization temperature on porosity observed Sun et al. for HC produced from ginkgo leaves with different microstructures. The HRTEM captures showed that highly disordered structure changes to graphite-like by increasing pyrolysis temperature (Fig. 6c). For example, at 600°C HC presented a highly disordered structure having randomly aligned carbon lattice bands (Fig. 6c (a)), with more distinct carbon lattice bands with amorphous microcrystallites can be seen in samples pyrolyzed at 1000°C . The graphitic ribbons grow large with increasing temperature, and it revealed that graphitic degree significantly increases at high pyrolysis medium (over 2500°C). An in-depth analysis of these type microcrystalline structure and different sodium transfer behavior authors suggested an extended “adsorption-insertion” mechanism [157]. Zhu et al. reported that hard carbon synthesized from corn straw piths presented decreased content of hetero-atom functional groups (S, P) [159]. This is mainly associated with the ordered turbostratic structure formation at high-temperature carbonization.

5.3.2. Effect of high-temperature carbonization on electrochemical performances

Varying the precursors, the reversible capacity can be increased by controlling the carbonization temperature in the range of 1300 – 1600°C , reaching about 300 mAh g^{-1} and the resulting ICE is improved to 80% . From the literature, it is suggested that HCs synthesized at this range of temperature usually provide high capacity, although more elaboration is needed to have better capacity retention. The majority of the electrochemical features is that a large portion of the capacity is obtained on the plateau region, while there is a small contribution on the slope region for the HCs carbonized at high temperatures of carbonization. Such property would be related to the reduced hetero atom content and defect sites of HCs.

Wang et al. studied possible three reasons for the capacity limit in HC derived from rice husk: degree of graphitization, defects, and presence of nanovoids. Owing to a large number of nanovoids, the samples are less dense, and these holes are large enough to accommodate sodium ions [158]. As a result, the sample carbonized at 1600°C delivered a maximum reversible capacity of 276 mAh g^{-1} [158]. As-prepared HC from lotus stems delivered 350 mAh g^{-1} with good capacity retention (94%) for 450 cycles, as demonstrated by Zhang et al. [139]. They suggested that, with increasing carbonization temperature, open pores turned into closed pores. As a result, the sodium storage of lotus stem-derived HC was related to the Na^+ adsorption in the defect sites and deposition of Na ions near closed pores. Subsequently, it promotes the plateau capacity which directly has an impact on increased electrochemical performance [139].

At higher carbonization temperatures, the structure of HC becomes more ordered and has increased turbostratic agglomeration of carbons, resulting in lower surface area and pore volume values, but a higher graphitization degree (See Table 4). HC synthesized at high temperatures exhibits a high specific capacity on the plateau region and a small contribution on the slope region. As the carbonization temperature increases, open pores turn into closed pores, which affects sodium storage. It is recommended to control the carbonization temperature within the

Table 4

Physical properties of HCs pyrolyzed at medium temperatures.

Precursor	Pyrolysis temperature	SBET [$\text{m}^2 \text{ g}^{-1}$]	I_D/I_G	d_{002} [nm]	L_a [nm]	L_c [nm]	References
Rice husk	1600	218	1.18	6	7.14	5.12	[158]
Lotus stem	1400	24.37	–	3.61	14.35	0.79	[139]
Corn straw	1400	25	–	–	–	–	[159]
Mangosteen shell	1500	8.9	0.66	12	2.93	1.64	[95]

range of 1300–1600 °C to improve the reversible capacity and resulting ionic conductivity efficiency (ICE) of HC (Fig. 6d and e). The complex physical and chemical properties of HC materials are closely related to the carbonization temperatures during the preparation. Precise quantification of HC characterization such as the *d*-spacing of the graphitic microcrystallites, surface area, and pore volume is crucial for a better sodium storage capacity and diffusion, which would facilitate further progress in this field. Generally, as shown in Fig. 7 hard carbon materials derived at medium temperatures ranging from 1200 °C to 1400 °C are considered to possess the most suitable structural properties, which can enhance the performance of sodium-ion storage in battery cells.

6. Heteroatom-doped biowaste-derived HC

Recently, significant attention has been paid to enhancing the sodium storage capability of HCs, emphasizing the effect of uniqueness, morphologies, and heteroatom doping on carbon precursors. Several heteroatom-doped HCs are derived from biowaste and have been investigated as anodes for SIBs. Adding heteroatoms to carbonaceous anode materials is an efficient method for improving electrochemical characteristics, surface wettability, electronic conductivity, charge transfer, and electrode/electrolyte interaction. Nitrogen (N), boron (B), sulfur (S), and phosphorus (P) are the most common dopants as heteroatoms. Nitrogen and boron dopants are substitutional dopants, meaning that they substitute carbon atoms in the lattice. By contrast, sulfur and phosphorus dopants are interstitial dopants introduced into the interlayer spaces [160].

6.1. Phosphorous doped hard carbon

Phosphorus has a greater atomic radius and stronger electron-donating potential in comparison with nitrogen and sulfur. In general, three valence electrons of a P atom contribute to establishing three σ -bonds with nearby carbon atoms to produce sp^3 hybridization. At the same time, the unpaired *p* orbital modifies the spin density slightly, possibly resulting in the enhancement of sodium storage. Doping with phosphorus could effectively extend the interlayer distance, which is beneficial to the transport of sodium ions. Additionally, it improves the electron transfer between Na and phosphorous-bonded carbon, increasing Na + adsorption. Nevertheless, large structure distortion may have a negative impact on the anode cycling performance. According to the computational study conducted by Qiao et al. phosphorus doping help to achieve a well-ordered structure (Fig. 8a) with increased interlayer distance, reduced ion transfer resistance, and encouraged the intercalation/extraction of sodium ions during cycling [161]. As a

result, phosphorus doping enhanced sodium storage by exhibiting the reversible capacity of 270 mAh g⁻¹ [161]. Alvin et al. prepared phosphorus-doped hard carbon by simply immersing lignin in phosphoric acid at different concentrations and pyrolyzing the sample at 1300 °C [162]. By increasing the P doping level from 0.72 to 1.10%, the interlayer distance between the graphene sheets was also enlarged from 0.375 nm to 0.387 nm. The -P-O bond was determined to be the dominant chemical species in the plane of P-doped HC that increased interlayer spacing. According to the electrochemical performance, P-doped hard carbon exhibited substantially higher plateau capacity (223 mAh g⁻¹) than undoped hard carbon (183 mAh g⁻¹) because of decreased defects, micropores, and central -P-O bonds [162]. Yan et al. [163] developed a new strategic synthesis method with ultrahigh phosphorus doping levels (Fig. 8b). HC was produced by mixing two miscible liquids PCl₃ and C₆H₁₂ as P and C sources, respectively, then the liquid mixture was simultaneously carbonized, and *in-situ* doped using nitrogen bubbling in an oxygen-free system. The mass loading of the phosphorus reached almost 30 wt%, which is significantly higher than previously reported P-doped carbon materials. Internal phosphorus atoms are mostly integrated into the carbon groups by generating P-(C₃) protrusions. Additionally, some parts of them can be joined to another P-(C₃) protrusion in a neighboring lattice through an interlayer PP bond. Anode material delivered a high reversible capacity of 510 mAh g⁻¹ at 100 mA g⁻¹. From material characteristic analysis, this superior behavior is attributed to the increased interlayer spacing, elevated adsorption energy, and a large amount of active site for sodium ion provided by P-(C₃) protrusions [163]. Wang et al. [164] synthesized P-doped hollow carbon nanorods by mixing red phosphorus powder and 1,8-naphthalene dicarboxylic anhydride (NDIA) and carbonizing them at 700 °C. Adjusting the mass proportion of red phosphorus compounds can maximize the sodium storage capacity of HC by controlling the microstructure and surface phosphorus configurations. There was a direct connection between electrochemical performance and phosphorus bonding. As calculated by DFT analysis, the P-C and P=O exhibited high sodium adsorption energy [164].

In general, the introduction of phosphorus doping has a beneficial impact on capacity. Nevertheless, it's important to note that the phosphorus content should not exceed 1 wt%. When there is a substantial quantity of phosphorus present in HC, a portion of the delivered capacity originates from the phosphorus itself.

6.2. Sulfur-doped hard carbon

Sulfur has a much higher covalent radius and, in most situations, thus can extend the graphene layers, allowing ready accommodation of

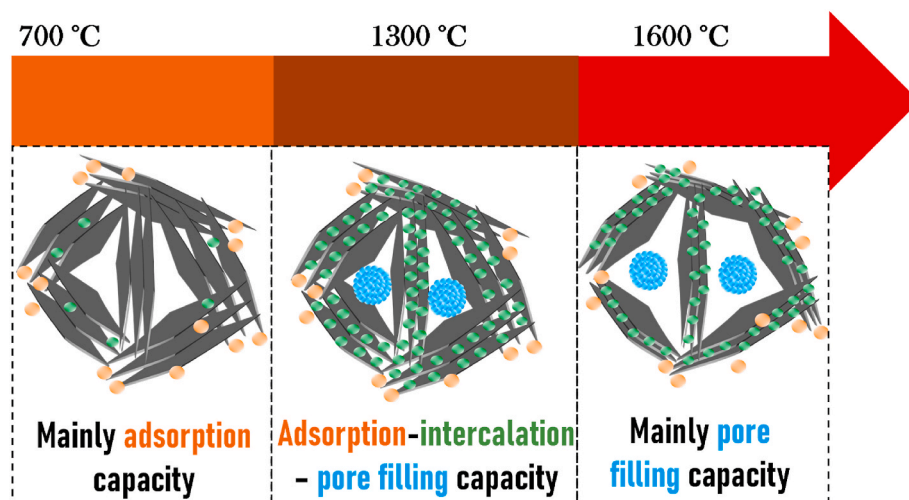


Fig. 7. Schematic illustration of sodium ion storage at different carbonization temperature.

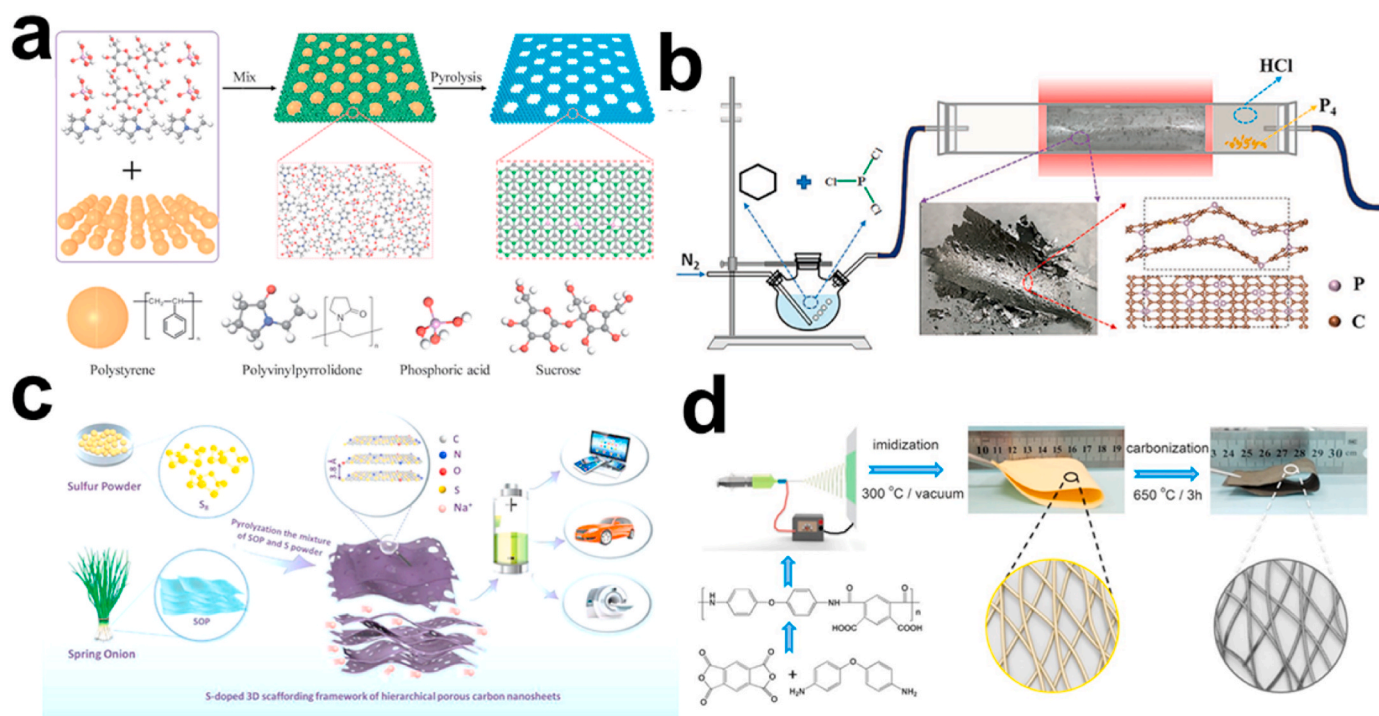


Fig. 8. (a) Schematic illustration of the synthesis for well-ordered 3D porous phosphorus-doped carbon. Reproduced with permission [161]. Copyright 2019, Royal Society of Chemistry. (b) Schematic illustration of the synthesis of UPCs. Reproduced with permission [163]. Copyright 2021, Wiley. (c) Schematic illustration of the synthesis of the 3D scaffolding framework of S-doped carbon nanosheets and their application for SIBs. Reproduced with permission [167]. Copyright 2019, Elsevier. (d) Schematic illustration of the fabrication of highly flexible carbon nanofiber films. Reproduced with permission [168]. Copyright 2015, Wiley.

sodium ions. Furthermore, the sulfur assists the adsorption of sodium ions to improve the sodium storage capability and contribute to electrical conductivity as well (Fig. 8c) [165,166]. The elemental sulfur is a source that is easily carbonized with hard carbon precursors.

Zhao et al. synthesized biomass-derived S-doped carbon nanosheets (S-CNs) by mixing spring onion peel as a biomass precursor with elemental S (Fig. 8c) [167]. This study described an eco-friendly, simple, and effective method for producing high-performance S-doped hierarchical porous carbon sheets. The high heteroatom-doping level, hierarchical porous structure, increased interlayer spacing, improved electrical conductivity, and wettability make a convenient path for Na^+ diffusion and a robust host for Na^+ insertion/extraction. As a result, S-doped HC can give high reversible capacities of 601.2, 545.2, 220.1, and 133.6 mAh g^{-1} at 0.05, 0.1, 5, and 10 A g^{-1} , respectively. These results are substantially greater than those of undoped samples [167].

When it comes to sulfur doping, much like phosphorus doping, a small quantity of sulfur has a favorable impact. Nevertheless, when the sulfur content is elevated, the capacity will primarily be obtained from the sulfur itself rather than the hard carbon.

6.3. Nitrogen-doped hard carbon

For improving the energy storage of SIBs, the nitrogen-doped hierarchical porous carbon has been efficiently investigated (Fig. 8d) [168–170]. Due to their ease of synthesis and fabrication method, the N-doped HCs are the most commonly investigated heteroatom-doped carbonaceous anode materials for SIBs [171]. This doping type can improve electrochemical performance, conductivity, surface wettability, and interlayer spacing. Nitrogen can also provide more extrinsic defects, allowing for the adsorption of more sodium ions [172].

Yan et al. synthesized nitrogen-doped porous carbon from bamboo leaves by an acidic etching process in an HF solution [173]. The obtained hard carbon had a unique sheet-like porous nanostructure, high surface area, and characteristic high nitrogen content. The porous

structure could provide suitable pathways for Na^+ diffusion/absorption and minimize volume expansion of electrode material during the charge-discharge process, which may lead to excellent electrochemical performance, including higher specific capacity and long cycle stability [173]. Also, XPS analysis revealed the presence of pyridinic nitrogen, which can also enhance capacity due to the free p-electrons in the outermost shell of pyridinic nitrogen and improve carbon conductivity. On the other hand, the pyridinic N can cause significant defects in carbon materials, resulting in mass open channels that allow Na^+ to be stored and transported simultaneously [174]. Yang et al. reported a novel concept for synthesizing nitrogen-doped carbon sheets (NDCS) derived from okara with higher nitrogen content [175]. The synthesis method was based on treating with a carbonization process followed by exfoliation. The obtained NDCS material had a lamellar structure. More loosely packed graphitic sheets were observed from TEM analysis, which provides a sufficient region for the electrochemical Na^+ de/intercalation reaction. Ion and electron diffusion were improved in N-doped carbon-based materials compared to bare carbon materials, resulting from the high electrical conductivity [175]. The obtained NDCS demonstrated unusually high coulombic efficiency (nearly 100%) and has high capacities (292.2 mAh g^{-1}) with an extremely long cycle life (2000 cycles) [175].

In general, nitrogen doping enhances capacity by boosting the adsorption of Na^+ ions. It has been observed that the capacity predominantly arises from the sloping region rather than a plateau region. To enhance capacity at the plateau region, raising the carbonization temperature is necessary. However, as previously discussed, high temperatures lead to a significant reduction in nitrogen content. An alternative could involve post-doping for the purpose of enhancing the doping effect.

7. Conclusions and perspective

The study of SIBs has grown due to the necessity to develop an

inexpensive and abundant alternative for LIBs. Moreover, significant effort has been invested in searching for the best electrode materials, with a large number of materials demonstrating sodium storage activity. A variety of carbonaceous materials with different structures have been investigated for application in anode materials, with some crucial outcomes suggesting that HC could be a suitable anode for SIBs. This is because sodium ions can be intercalated into its the graphite layers by increasing the interlayer distance or via co-intercalating sodium ions with the solvent molecules. Due to the differences in microstructure and sodium storage mechanism, hard carbon materials exhibited higher specific capacities than graphite.

In this review, we summarized three main types of bio-waste precursors for HCs along with their preparation conditions and demonstrated that HC materials can be effectively synthesized using simple carbonization techniques with mentioned inexpensive and readily available precursors. By altering the processing conditions such as annealing temperature, their primary features, including porosity, structure, surface chemistry, and defects may be easily modified. Moreover, the electrochemical properties of HC were also analyzed by the range of carbonization temperatures.

In general, the structure/performance relationship was investigated in-depth, and the following trends were observed for biomass-derived HCs: increasing the pyrolysis temperature would decrease the inter-layer distance, defects, impurity, and surface area; but it will increase the number of stacking layers and the number of internal pores. As a result, the proper choice of annealing temperature for certain types of HC and a delicate balance of surface/structure characteristics could yield promising anode material with enhanced ICE, improved rate capability with good cycling performance. Next, to further optimize the HC property, the effect of doping with sulfur, nitrogen, and phosphorus of bio-wastes was discussed in detail. The addition of heteroatoms might significantly improve the electrochemical performance in terms of specific capacity and initial coulombic efficiency. However, it can also increase the content of voids and increase specific surface area with low ICE. Hence, balancing the number of heteroatoms is important to obtain desired electrochemical and material properties. In addition, the sodium storage mechanism in HC was also summarized and discussed, as it has become an ongoing hot topic due to the controversial results regarding the Na^+ -insertion in the two-voltage region.

Due to the recent commercialization of the SIBs and mass production targeting in 2023, this review can be helpful for the further development and optimization of SIBs, as there is still room to produce HC with superior behavior and performance. Regarding the properties of HCs, due to their poor crystallinity and porosity, characterizing the structure and porosity of hard carbon materials remains difficult. A deeper understanding of sodium ion accumulation and its diffusion will contribute to the progress in this area by resolving these shortcomings of HCs.

Another challenge of bio-waste-derived hard carbons is low ICE which needs to be improved. In general, a higher coulomb efficiency than 90% is required for practical application. There are optimization strategies to resolve including optimization of electrolytes and additives to build a stable SEI layer that is important for the performance of HC anodes; surface modification to reduce irreversible Na^+ surface reaction (surface coating or usage of a different carbonization atmosphere); in-depth understanding of the sodium ion storage mechanism is required for hard carbon anode materials derived from biomass, as there are differing views on the sodium storage mechanism of hard carbons.

A better understanding of these points may provide an improvement for future preparation methods to enhance the electrochemical performance of HC materials. For bio-waste precursors, it is recommended to perform carbonization at a temperature between 1300 and 1400 °C in order to achieve a capacity of around 280 to 320 mAh g⁻¹ at this temperature range. Moreover, understanding and *in situ* formation of closed nanopores with inorganic impurities are essential to enhance electrochemical performance. The discovery revealed that the formation of closed nanopores has a beneficial impact on the capacity of hard carbon

[176,177]. The development of characterization methods for investigating the properties of HCs specifically the closed nanopores will be necessary to understand their mechanism and further optimize their characteristics, paving the way for their widespread commercialization and technological development of SIBs. As Prof. Donald Sadoway says: "If you want to make something dirt-cheap, make it out of dirt. Preferably dirt that's locally sourced" [178].

CRediT authorship contribution statement

Lunara Rakhyimbay: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Data curation, Conceptualization. **Nardana Bazybek:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Kenes Kudaibergenov:** Methodology, Investigation, Data curation, Conceptualization. **Seung-Taek Myung:** Writing – review & editing, Writing – original draft, Visualization, Validation, Conceptualization. **Zhumabay Bakonov:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Conceptualization. **Aishuak Konarov:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Funding acquisition, Data curation, Conceptualization.

Declaration of competing interest

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

Data availability

Data will be made available on request.

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