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Pristine and engineered biochar as Na-ion batteries anode material: a comprehensive overview

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Abstract

The sodium-ion battery (Na-ion battery, NIB) is considered the most promising post-lithium energy storage technology, taking advantage of using the same manufacturing technology as Li-ion batteries (LIBs), while enabling the use of abundant and economic, thus more sustainable raw materials. Due to the inability of Na^+ ions to be intercalated within the graphene layered structure of graphite-based electrodes, the state of art anode material in LIBs, highly disordered and microporous carbons, known as hard carbons, are considered the anode material of choice for NIB technology. Biomass-derived biochar (BC) is one of the most relevant classes of hard carbons, exhibiting a good combination of sustainable fabrication, structural-morphological features and electrochemical performances. In this review, the main achievements on BC are rigorously reported from the production to the application into NIBs, with particular emphasis on the strategies to improve the electrochemical behaviour through activation and tailoring its chemical and structural properties. These strategies include selecting specific feedstocks, modulation of the pyrolysis temperature, pre- and post- production treatments, and materials engineering. The possible role of BC in sustainable NIBs development is also briefly discussed, together with some insights of its use in other post-Li energy storage systems and some conclusion remarks and future direction of the research.

Keywords: biochar; hard carbon; anode; sodium ion battery; sustainable energy

Acronyms and Abbreviations

ATR	Attenuated total reflectance
BC	Biochar or biomass-derived carbon
BES	Broadband electrical spectroscopy
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
CE	Coulombic efficiency
CNT	Carbon nanotube
COP26	2021 United Nations Climate Change Conference
CRM	Critical Raw Material
CV	Cyclic Voltammetry
CVD	Chemical Vapour Deposition
CVF	Crystalline volume fraction
DFT	Density functional theory
DMA	Dynamic mechanical analysis
DRIFTS	Diffuse reflectance infrared Fourier transformed spectroscopy
EIS	Electrochemical Impedance Spectroscopy
ESR	Electron spin resonance
EPR	Electron paramagnetic resonance
EV	Electric Vehicle
FT-IR	Fourier transformed infrared spectroscopy
GCMC	Grand Canonical Monte Carlo
GHG	Greenhouse Gas
H/C	Hydrogen/Carbon
HC	Hard Carbon
IPCC	Intergovernmental Panel on Climate Change
KIB	K-ion battery, potassium-ion battery
LIB	Li-ion battery, lithium-ion battery
Li-O_2	Lithium-Oxygen or Lithium-air battery
Li-S	Lithium-Sulphur battery
MD	Molecular dynamics
MDSC	Modulated Differential Scanning Calorimetry
MOF	Metal Organic Framework
NIB	Na-ion battery, sodium-ion battery
Nitrogen, oxygen and phosphorus co-doped biochar	
O/C	Oxygen/Carbon
PDFs	Pair distribution functions
RS	Reflectance spectroscopy
SEI	Solid Electrolyte Interphase
ReaxFF	Reactive force field
SHE	Standard Hydrogen Electrode
UV	Ultraviolet
XAS	X-ray absorption spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

1. Introduction

One of the bold and transformative steps being urgently needed by our modern society to face the dramatic worldwide consequences of climate changes, thus shifting the world onto a sustainable place, is the transition from mobility based on fossil fuels to electric vehicles (see the UN 2030 Agenda for Sustainable Development or the European Green Deal) [1]. Accordingly, the development of new generation electrochemical storage systems has become a crucial task to be accomplished in the near future. During the last decades, lithium-ion batteries (LIBs) have gained the attention of both academia and industry, spreading from laboratory to almost every high-tech device [2, 3]. As a direct consequence, lithium reserves are becoming shorter year by year, and their price is rising at the same time [4]. Therefore, the need for post-LIBs technologies is increasingly more compelling, and sodium-ion batteries (NIBs) are among the most promising systems, considering that Na is widely abundant, equally distributed on Earth, and exhibits similar chemistry to that of Li; some limitations to NIBs development are constituted by the need of new specific materials for the electrodes, the energetically less favourable intercalation of Na^+ into a fixed positive electrode with respect to Li^+ (limiting the overall cell voltage and, hence, the energy density), slower kinetics, possible side reactions with the electrolyte (limiting the cycle stability), generally lower initial coulombic efficiency and higher cell volume expansion [5-8]. In recent years, the technological gap between LIBs and NIBs has been narrowing, with many companies (Novasis Energies, Faradion, Natron Energy, Rechargion Energy, HiNa, Altris, TIAMAT, AGM, Contemporary Amperex Technology Co., Ltd. - CATL) declaring to be close to commercialization of NIBs [9-11], as summarized in Table 1 [12]. Most notably, Northvolt (Sweden) announced at the end of 2023 of having officially inserted into its cell portfolio a sodium-ion battery based on Altris AB technology, enabling the worldwide expansion of cost-efficient and sustainable energy storage systems to afford the expected global electrification based on renewable power sources [13].

Table 1. List of the companies working on the commercialization of NIBs, adapted and reproduced from Hasa et al. [12].

Company	NIB Cell Positive // Negative	Current Wh/kg	Available Formats	Expected Markets
Faradion (UK), AMTE (UK), INDI-Energy (India), Natrium Energy (China)	Na Layered Oxide // HC	120-160 135-140 120-150 130-160	Pouch, Prismatic	Energy – including Telecoms, mobility, back-up, UPS, ESS, Renewables
HiNa Battery (China)	Na Layered Oxide // Soft Carbon	120-145	Pouch	Energy - mobility, back-up, UPS, ESS, Renewables
CATL (China)	Prussian-White Analogue // HC	160	Pouch	Grid, stationary, UPS
Tiamat Energy (France)	$Na_3V_2(PO_4)_2F_3$ // HC	80-100	Cylindrical	Power markets, hybrid buses, Power tools
Altris AB (Sweden)	Prussian-Blue Analogue // HC	100-120	Pouch	Energy markets
Natron Energy (USA)	Prussian-Blue Analogue: Fe // Mn	25-40 (50Wh/l)	Pouch	Data centres, back-up

On the positive electrode side, many different chemistries are considered, including layered transition metal oxides, Prussian white, or vanadium phosphate, on the negative electrode side, hard carbons have shown the best combination of performances and workability [14-17]. In particular, the carbon produced by biomass pyrolysis, known as biochar (BC), represents a solution that combines a sustainable productive methodology and good electrochemical behaviour [18-20]. BC properties must be finely tuned to match the requirements of marketable energy storage devices. Due to the great variety of BC production and tailoring approaches, the need of a comprehensive overview on the use of BC as anodic material for NIBs is crucial, aiming at considering all the possible strategies proposed in literature.

As reported in Figure 1S, the interest of the scientific community on BC applied to energy storage is exponentially growing from about 2015, mostly related to the development of NIBs, but in part also to the development of other post-Li technologies.

Despite some reviews have already pointed out the beneficial role of biochar in energy storage devices [18, 19], the scientific literature on this topic still suffers the lack of uniformity among the reported studies in terms of prepared materials, post-synthesis treatments, and conditions of electrochemical

testing, thus constituting an obstacle for all the researchers who are going to approach it for the first time. Therefore, this review article aims at systematically discussing the application of biochar into NIBs and other post-Li technologies, comparing as much as possible the results obtained by different research groups and extrapolating the correlation between the chemical and structural properties of the materials and their electrochemical performances, so that it could serve as a guideline for further discoveries and developments.

2. BC production and engineering

2.1 BC production

BC is produced through thermochemical cracking of biomasses under different conditions. The main routes for BC production are torrefaction, pyrolysis and gasification. The main and more relevant difference between these above-mentioned routes is represented by the different temperatures reached during the process.

During torrefaction, the temperature rises to 200-350°C achieving only partial carbonization of biomass [21]. Solid recovered from biomass torrefaction generally presents a content of up to ≈ 50 wt.% with a yield of up to 70% [22]. An improved yield of up to 80 wt.% can be reached using microwave heating and additives [23-25]. The technology hardly met the requirement to produce effective anodic materials due to the lack of conductivity.

Increasing the processing temperature above 400°C, proper pyrolytic processes occur in an oxygen-free atmosphere. While torrefaction promotes a slight degradation of biomass macromolecules, pyrolytic conversion leads to an advance cracking process of lignin, cellulose and hemicellulose with the formation of BC and complex liquid mixtures named bio-oils [26]. Pyrolysis could be run by using different heating technologies [27-29], and apparatus designs [30] with wide variations in product fraction yields quality [31].

Contrary to pyrolysis, gasification occurs in an oxidant atmosphere such as air [32], oxygen or steam [33], generally at temperatures higher than 800°C with or without the addition of a catalyst [34]. The main gasification output is represented by gas composed of a mixture of carbon monoxide, carbon dioxide, methane, hydrogen and water vapour. Contrary to BC produced from pyrolytic conversions, carbon recovered from stoichiometric gasification is generally very rich in ash and poor in carbon content, discouraging its use for battery applications.

The choice of BC productive way is strictly related to the final use that could require a greater o lower presence of oxygen and hydrogen content, accordingly to Van Krevelen graph as shown in Figure 1.

The structure of BC produce using lignin, sewage sludge, and wood is closely related to both temperature and heating rate. A productive temperature of only 500°C leads to high H/C and O/C ratios, avoiding using these chars for possible development of anode materials. The carbon content is not the only BC feature relevant to electrochemical applications. Another key parameter is represented by the defective degree of the carbon matrix.

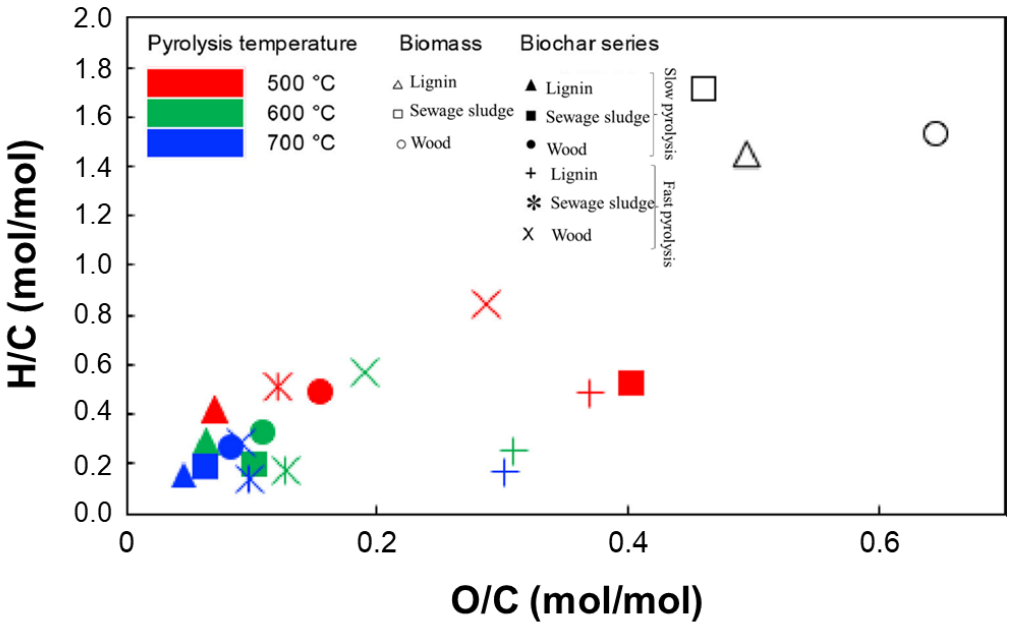

Figure 1: Van Krevelen diagram showing the effect of processing temperature on BC. Picture readapted and reprinted with permission (CC BY-NC-ND 4.0) from Bartoli et al. [35].

Carbon defectiveness could be quantified by comparing a carbon sample to a perfect graphite and estimating the different arrangements of graphitic domains through several techniques, such as Raman spectroscopy [36], transmission electron microscopy [37] and x-ray powder diffraction [38]. Considering BC thermal evolution, three main stages could be identified and correlated with processing temperature, as sketched in Figure 2.

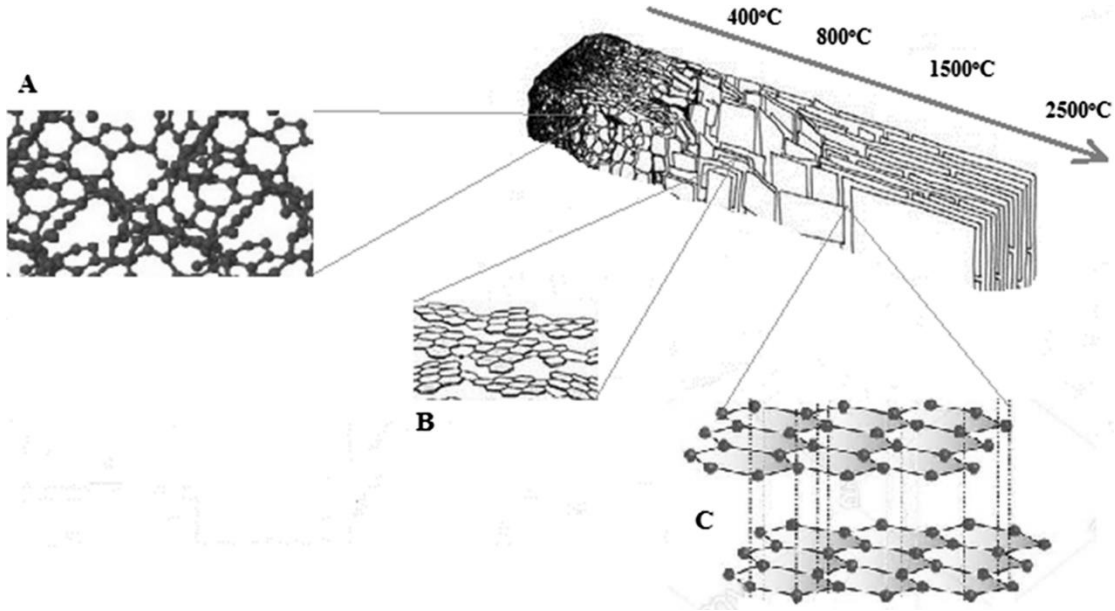

Figure 2: Thermal evolution of BC structure considering (A) totally amorphous materials produced at low temperature, (B) hard carbon produced from 800°C and (C) soft carbon produced by using high annealing temperature. Picture was reprinted under CC BY 4.0 license from Tomczyk et al. [39].

First, biomass undergoes proper carbonization at a temperature ranging from 300 to 400°C with cracking of its components through complex reaction routes and forming the first aromatic units and releasing small gaseous molecules as H_2O, CO_2 and N_2. In this stage, BC is massively tailored with oxygen-based functionalities (*i.e.*, hydroxyl, carbonyl and carboxylic residues) and displays a highly defective carbon structure. By increasing temperature between 600 to 800°C, aromatic structures further condense forming proper graphite-like domains still highly disordered but with lesser residual groups. These materials are commonly classified as hard carbon due to their high mechanical hardness [40].

Further temperature increments lead to a progressive enlargement and ordering process of graphitic domains through turbostratic rearrangement [41] that end at a temperature close to 3000°C when the maximum graphitization degree is reached [42].

The thermal evolution of BC could easily be evaluated by using Raman spectroscopy. Raman spectroscopy is widely utilised to quickly and non-destructively characterise all carbons as they are featured by peculiar and distinct spectral fingerprints [43-45]. Usually, their structural and bonding properties are investigated by studying the scattering excited by a given laser wavelength, whereas complementary information on some specific aspects is inferred by multi-wavelength [46-48].

Visible light (with a wavelength of 532 or 633 nm) is commonly used to carry out single-wavelength Raman analysis [40]. Since the cross-section for sp^3 C–C vibrations is negligible for visible excitation, the visible Raman spectra of carbon materials with mixed sp^3/sp^2 bonding nature are dominated by sp^2 contributions [49]. This is the reason why the nanocrystalline,

disordered/amorphous and hard carbons, all containing graphitically ordered nanodomains, exhibit similar visible Raman spectra, consisting of two broad features, the well-known D- and G-bands [50-54] centred around to 1340 and 1580 cm^{-1}, respectively [49, 55].

Since the frequency, width and relative intensity of the two bands are sensitive to bonding strength, distribution of bonding lengths and angles, nature and density of defects, Raman spectroscopy is often used, together with complementary characterization techniques, such as transmission electron microscopy[56], to monitor the changes in the microstructure of the graphite-like carbons produced by the variation of their preparation conditions. In order to qualify the nature and quantify the density of defects, the D/G intensity ratio (I_D/I_G), calculated by spectra fitting [36, 57, 58], is used to estimate the average size of graphitically ordered domains (L_C), *i.e.*, the coherence length [55] that gives a measure of the inter-defect in-plane distance [59].

For hard carbons, the carbonisation temperature (up to 1500°C) causes the width of the D- and G-bands to decrease and I_D/I_G to increase [51, 54, 60, 61]. As they contain randomly-stacked highly-disordered turbostratic graphitic nanodomain regions cross-linked by amorphous regions with sp^3 bound sites [62, 63], these spectral changes are indicative of the narrowing of the distribution of bonding lengths and angles and of the conversion of non-sp^2 to sp^2 defects [47, 64], which only contribute to the D-band intensity, *i.e.*, of the evolution towards a less disordered structure, with increased probability of finding sixfold rings in the C clusters [49]. At high carbonisation temperatures, increasing carbonisation time causes only I_D/I_G to decrease [54]. This signals the increase of L_C, *i.e.*, the reduction of the density of sp^2 defects in the basal planes, resulting in higher graphitisation degree/development of the turbostratic graphitic nanodomains [65].

The details of the short-range crystal structure of the BCs are extremely important to prompt a facile and reversible uptake of Na^+ species in the anode of a sodium-ion battery. The distance between the graphitic layers of a BC is larger than that of conventional graphite allowing the reversible intercalation/de-intercalation of bulky Na^+ species. Such *"larger"* distance can be established by a variety of approaches, including: (i) pre-oxidation of the BC [66]; or (ii) introduction of bulky heteroatoms (*e.g.*, P) in each graphitic layer [67] or of nanometric templates (*e.g.*, MgO) between the graphitic layers [68]. X-ray diffraction is a very suitable technique to gauge the distance between the graphitic layers in a BC. Such distance is evaluated by determining the (002) interplanar spacing using the Bragg's equation [69]. Other important structural parameters of the BC are the correlation length along the c-axis (L_c) and the correlation length along the basal plane (L_a), which are evaluated with the Scherrer's equation starting from the (002) and (100) reflections, respectively [70]. Such parameters allow the size determination of the ordered domains in bulk BC and thus gauge whether the BC is amorphous, turbostratic (small size of the ordered domains; it is also known as *"hard*

carbon") or graphitic (large size of the ordered domains) [71]. It was shown that Na^+ uptake in BC anodes is favoured by an amorphous/turbostratic structure due to the more facile accommodation of Na^+ species at the defect sites [72, 73]. A preliminary assessment of graphitization of BC could be done through Fourier transformed infrared (FT-IR) spectroscopy aiming at identifying hydrogen, oxygen and nitrogen containing functional groups and providing very useful information concerning the degree of graphitization of the carbon matrix [74-76]. Nevertheless, a significant drawback of BC is related to its great IR absorption that can be limited by using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) [77] and total internal reflectance (ATR) [78] approaches.
The other relevant properties of BC, such as porosity and specific surface area, will be discussed in the next sections.

2.2 BC post-production modification

Pristine BC could not meet the bulk and surface properties required for the electrochemical applications (*i.e.*, surface area, porosity, chemical functionalities) [18, 79]. Accordingly, several chemical and physical procedures could be implemented to tune BC properties acting on the surface and bulk features. In the following sections, the main routes for tailoring BC properties are systematically discussed.

2.2.1. BC surface tailoring

The functionalization of carbonaceous materials is a well-established practice for producing a wide range of tailored materials. Nowadays, surface texturing with nanostructures represents the core productive step for the realization of catalysts [80], absorbers [81] and multifunctional compounds [82, 83]. As summarized in Figure 3, this process is mainly achieved by dispersing inorganic species on the surface, even if carbon-on-carbon decoration could also be performed.

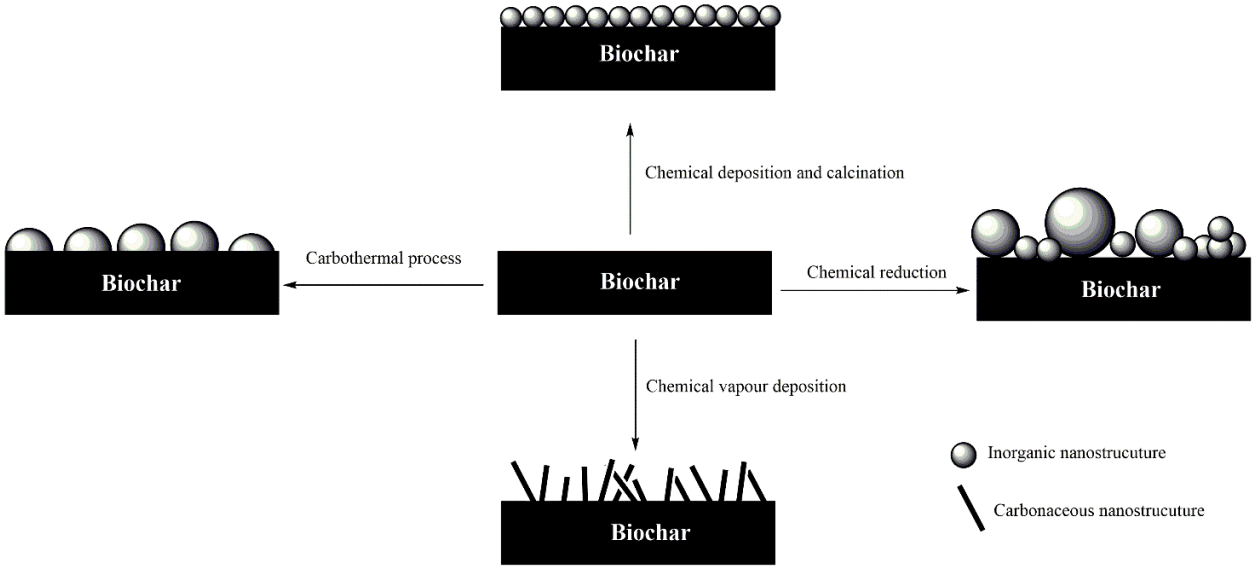

Figure 3: Summary of surface tailoring routes to produce modified BC.

Carbon-on-carbon tailoring is uncommon in BC tailoring as it is more suitable for high-tech materials, such as carbon fibres [84] or graphene [85]. Zhang et al. [86] reported a chemical vapour deposition (CVD) approach for the growth of carbon nanotubes (CNTs) on nut shell derived BC. This study leads the way in using CNTs-modified BC to produce electrodes used for LIBs [87] and supercapacitors productions [88]. Bartoli et al. [89] reported a solvent mediated process for tailoring the surface of micrometrical BC spheres produced by pyrolysis of cellulose nanocrystals. Authors described a variety of carbon-carbon decorations on BC surfaces ranging from needles to nanospheres.

CVD is also used for the deposition of metal nanostructures onto several different types of matrices, such as polymers [90], CNTs [91] or carbonaceous feedstock [92]. Metal tailoring of BC through CVD is not well-established, and other routes are preferred.

Accordingly, inorganic tailoring of BC has become a well-established procedure for a wide range of applications, ranging from environmental remediation [93] to electrochemistry [94], by using deposition, chemical reduction, calcination and carbothermal reduction approaches.

Simple deposition of inorganic materials represents an affordable way to produce nanostructured electrodes, useful for biosensing [95] and electrochemical storage applications [96]. The main issue of the simple deposition is the lack of uniformity in the coating layer and its instability under working conditions. A calcination process could improve the adhesion of inorganic decoration without forming reduced material, as reported by Zeng et al. [97]. Similarly, carbothermal processes are used to anchor inorganic materials to the BC surface. Contrarily to calcination, carbothermal reduction involves the simultaneous reduction of inorganic precursor and oxidation of BC with a remarkable surface area increment according to the mechanisms summarized by Shen et al. [98]. The main

drawback of this approach is the possible alteration of BC morphology, as reported by Tamborrino et al. in the case of sponge-shaped coffee-derived BC and iron salts precursors [99]. Authors showed the disruption of micrometric particles, but this phenomenon was counterbalanced by the formation of well anchored iron nanoparticles covered by a thin layer of iron oxide. Alternatively, chemical reduction is another possibility to tailor the BC surface with regular metal-based micrometric and nanosized structures. The reduction process could be performed by using reducing agents such as sodium borohydride [100]. This approach generally leads to an inhomogeneous metal particle size distribution if surfactants are not used as additives [101].

Surface tailoring is not the only modification usually applied to tune the BC properties. The reactivity of BC graphitic-like domains represents a very attractive functionalization route, as summarized in Figure 4.

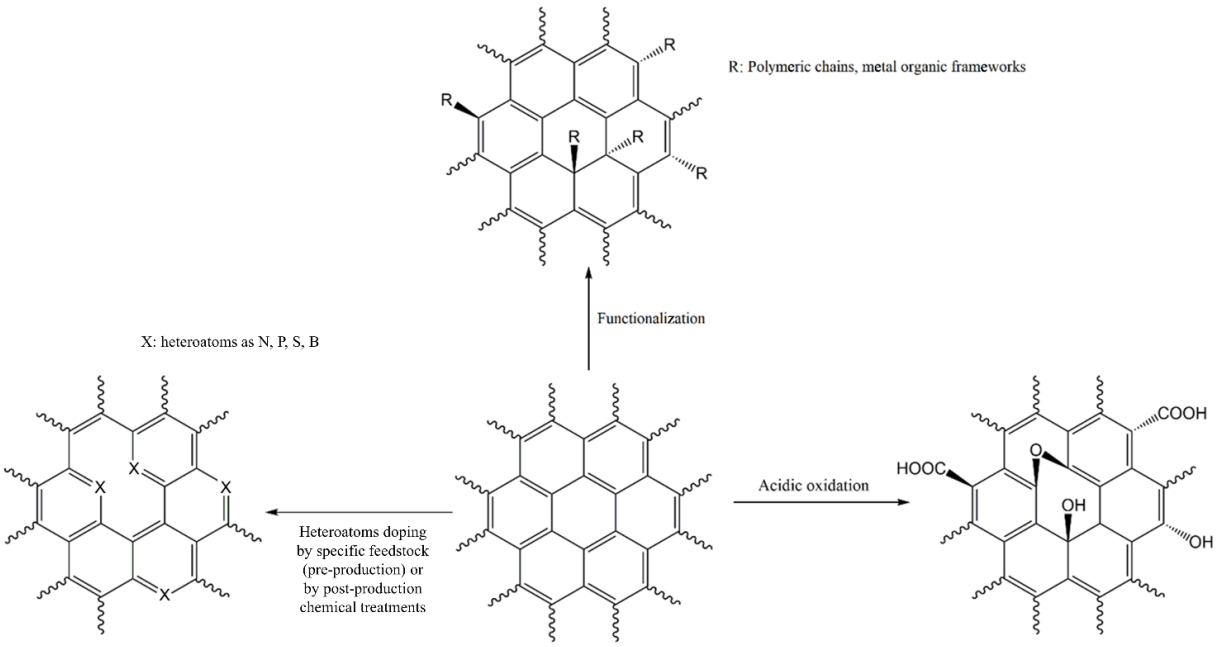

Figure 4: Summary of some possible functionalization introduced onto sp^2 domains of BC structures.

Heteroatom doping of BC is achievable by direct conversion of heteroatoms rich feedstock as in the case of N-doping of chitosan derived BC [102]. Doping carbon matrices with nitrogen, sulphur and phosphorous atoms yielding carbon nitride, sulphide, and phosphide functionalities is a well-known approach to modulate their electronic properties, chemical composition, defects, and vacancies [103-105]. The heteroatom functionalization thus acts to modify the surface wettability, electrochemical properties and electronic conductivity of BCs, facilitating the electrode/electrolyte interaction, charge transfer and reaction kinetics [104].

Alternatively, post-production procedures such as ball-milling [106, 107], urea impregnation, partial calcination [108], and acid wash could be used [107, 108]. Similar approaches could be implemented

to introduce P [109], S [110-112] and B [113] sites. BC conjugation with polymeric chains or metal organic frameworks (MOF) is used to both extend the solubility and dispensability range of BC particles and to tailor its chemical properties massively [114, 115]. Acidic treatments can introduce a wide variety of oxygen-containing groups, but they will be discussed in the following section, together with the other chemical activation processes.

Evaluation of the effectiveness of the tailoring process is crucial to make operative decision about the material performances. Several techniques could be efficiently used for determining the functionalization degree. Among them, X-ray photoelectron spectroscopy allows to determine the surface chemical composition of the BCs and the chemical states of the different surface elements [116]. XPS is extensively used in the literature specifically to identify the surface functional groups of BCs [70]. It is also used to: (i) gauge the degree of disorder of the carbon surface, being able to discern easily between its various hybridization states [117]; and (ii) detect the impurities (*e.g.*, K, Mg, Cl) on the BC surface, providing a facile avenue to evaluate the quality of the final material [118].

2.2.2. BC activation

Contrarily to surface treatment, activation processes are not used for tailoring the properties of nanostructured carbon materials such as graphene and CNTs but they are largely employed to improve the properties of BC [119] and coal [120]. Activation processes promote a large increment of surface area up to hundreds or thousands of $m^2\ g^{-1}$ [121] through physical or chemical degradation of carbonaceous structures, as discussed in the next sections.

Generally, electrochemical applications require electrode materials endowed with a high specific surface area in order to maximize the charge storage and effective reaction surface [122]. The specific surface area and porosity (*i.e.*, pore size distribution and pore volume) of BCs, or of any other solid material, can be determined by means of the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) analytical methods. These analyses consist in the adsorption and desorption of nitrogen, whose hysteresis isotherm curve shape is indicative of the type of pores present into the bulk material. Pores are classified on the basis of their diameter: materials can exhibit macropores (diameter > 50 nm), mesopores (2-50 nm) and micropores (< 2 nm) [123]. Normally, carbon nanomaterials exhibit a BET surface area of 500-1500 $m^2\ g^{-1}$, although functional compounds of 3400 $m^2 \cdot g^{-1}$ of surface area have already been synthesized [124]. In summary, nitrogen adsorption-desorption isotherms are crucial to estimate the porous structures and surface areas of BCs, giving a further tool for the comprehension of their electrochemical activity.

Physical treatments

Physical activations are high temperature processes taking place through the reaction of gaseous agent such as CO_2, H_2O or NH_3 with BC matrix at temperature higher than 800°C [125]. The most diffuse physical activation is based on the use of CO_2 as reported by many authors [125-127] according to the reaction reported in eq.1.

$$CO_{2(g)} + C_{(g)} \rightarrow 2CO_{(g)} \quad \text{eq. (1)}$$

This reaction has a ΔH of 40.79 kcal/mol [128] and promotes a very effective increment of surface area and porosity as reported by many authors [129-131]. CO_2-activation could be also enforced by using not only pure gas but also un-condensable pyrolytic gas and post-combustion fumes.
Alternatively, steam could be used as a replacement for CO_2 induced activation pathway, as reported in equation (2).

$$H_2O_{(g)} + C_{(g)} \rightarrow CO_{(g)} + H_{2(g)} \quad \text{eq. (2)}$$

Steam-activation has a lower ΔH of 31.14 kcal/mol [128] compared with CO_2-activation and it promotes not only the increment of surface area but also the removal of tar [132].
Physical activations are simple processes, easily scalable and based on the use of very cheap activation agents but require high energy inputs and long processing times [133].

Chemical treatments

Chemical treatments represent the other significant activation processes to increase BCs surface area and porosity. They can be regrouped into three main groups: i) alkaline, ii) acids and iii) oxidants-mediated processes.
Alkaline chemical activations are generally performed by using sodium or potassium hydroxide [134, 135] or carbonates [136-138], inducing a complex reactivity as reported in the following equations (3-8), where M = Na, K:

$$4MOH_{(s)} + C_{(s)} \rightarrow 4M_{(s)} + CO_{2(g)} + 2H_2O_{(g)} \quad \text{eq. (3)}$$

$$6MOH_{(s)} + C_{(s)} \rightarrow 2M_{(s)} + H_{2(g)} + 2M_2CO_{3(s)} \quad \text{eq. (4)}$$

$$M_2CO_{3(s)} \rightarrow M_2O_{(s)} + CO_{2(g)} \quad \text{eq. (5)}$$

$$4MOH_{(s)} + C_{(s)} \rightarrow 4M_{(s)} + CO_{2(g)} + 2H_2O_{(g)} \quad \text{eq. (6)}$$

$$4MOH_{(s)} + 2CO_{2(g)} \rightarrow 4M_2CO_{3(s)} + 2H_2O_{(g)} \quad \text{eq. (7)}$$

$$M_2O_{(s)} + H_2O_{(g)} \rightarrow 2MOH_{(s)} \quad \text{eq. (8)}$$

BC activation mediated by alkaline media occurs at temperatures higher than 700°C, but requires significantly less time than physical activation [121] and an acidic wash to remove all the inorganic species remaining after the process. As enlightened by the chemical reaction reported in eq.3, 5 and 6, CO_2 and H_2O formed as decomposition products of alkali medium could promote further activation reactions according to eq.1 and 2.

Acidic-mediated activation is generally performed using strong oxidant acids such as HNO_3 [139] or H_3PO_4 [140]. This approach requires a low temperature above 80°C and short reaction times [141], promoting, as shown in Figure 4, the insertion of oxygenated functionalities on the surface of BC.

The use of oxidant agents such as hypochlorite [142], persulfates [143, 144] or hydrogen peroxide [145] promotes an activation process very close to the one achieved by using acidic media.

3. BC as electrode material for sodium ion batteries

3.1. Sodium ion storage mechanism in BC

The anodic behaviour of any material for the NIBs mandatory requires a lower sodium ions intake and expulsion potential compared with metallic sodium. Noticeably, highly ordered graphitic materials could satisfy these condition for lithium but they cannot reach the same performances for sodium [146, 147].

As reported by Stevens et al. [148], highly graphitic carbonaceous materials cannot accommodate large amounts of sodium between the graphite layers with an expansion of the interlayer spacing, as in the case of lithium. This was due to the chemical potential of sodium that is lower than the one of the metal itself. Accordingly, metallic sodium is more energetically induced to electroplate on the surface of the carbon surface. An alternative to highly graphitic carbon, disordered carbonaceous materials known as hard carbons are solid alternatives for realising NIBs. These highly disordered materials contain nanoscale porosity formed by several graphene sheets piled and twisted. In hard carbon, sodium insertion also occurs in the nanopores with an adsorption process with a low voltage plateau in the potential/capacity curve. Authors observed that the sodium species in these pores have a chemical potential close to the metal itself.

Recently, Alvin et al. [149] evaluated the carrier-ion storage mechanism of Li^+, Na^+ and K^+ in hard carbons samples. This study showed improved adsorption of ions on the defective regions and the edges.

Among hard carbons, BC is the most suitable for the development of anodic materials for NIBs. BC presents small and highly disordered graphitic domains, even after annealing up to 1500°C [36], with micro-porosity that can receive and host Na^+.

Alvin et al. [150] explored the mechanism of sodiation of BC produced from lignin considering the Na^+ uptake on the edges and defect sites, on the interlayer space between graphitic layers and into micropores as reported in Figure 5.

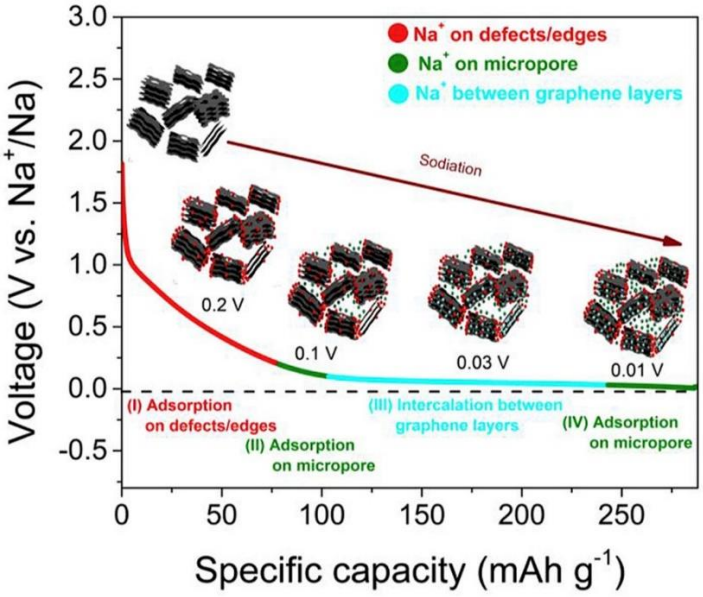

Figure 5: Sodiation mechanism in lignin derived BC. Reprinted with permission from ref. [150].

This mechanism was further studied by Gomez-Martin et al. [151] by investigating the mechanisms responsible for storage in low- and high-potential regions using olive stones-derived BC, produced using a pyrolytic temperature ranging from 800 to 2000 °C as reported in Figure 6. By means of deep characterization measurements, authors demonstrated that, for the material herein investigated, the sodiation mechanism proceeds though intercalation-adsorption instead of adsorption-intercalation. The correct mechanism assigned is still debated due to the large variety of materials that fall under the simple name of BC. Bommier et al.[152] suggest that insertion into defective sites is more impacting on the sodiation than the intercalation process. Some key points remain valid for any material studied, such as a positive correlation between the decrement of sloping capacity with increment of long- and short-range order of BC structure.

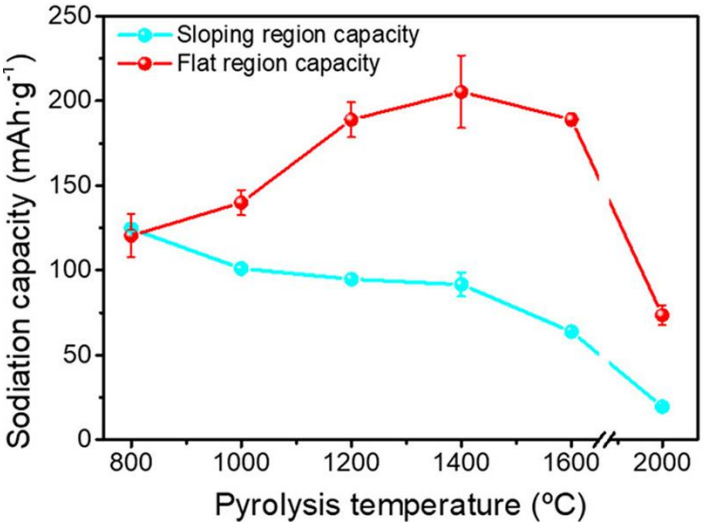

Figure 6: Sodiation capacity in hard carbons as function of pyrolytic temperature as reported by Gomez-Martin et al. [151] (Copyright © 2019 American Chemical Society).

Raman spectroscopy, which probes material properties on a shorter-range scale than XRD, could be performed on hard carbon-based electrodes to monitor the structural changes induced in the host matrix by sodiation/desodiation [63] and, more generally, by insertion/extraction of alkali metal ions [153]. Raman scattering can be measured after or before pulling out the electrode material from the electrochemical cell (*ex-situ* and *in-situ* measurements, respectively). The former measurements allow easily evaluating the reversibility of the Na^+ (Li^+/K^+) ion storage, even if some caution is needed as sodium deintercalates in air [63]. Different from *ex-situ* analysis, *in-situ* measurements require the use of special cells equipped with optical windows. By appropriately setting the measurements conditions, *in-situ* analysis can also be carried out during the electrochemical reaction (in *operando* conditions) to clarify the sodiation mechanism [63, 153, 154].

The storage mechanism of sodium in hard carbons has not been fully understood and is still a matter of debate. As comprehensively reviewed by Sun et al. [155], several models (such as "insertion-filling", "adsorption-filling", "adsorption-insertion", and "multistage mechanism") try to explain, through complementary analysis techniques, the sodiation process on the basis of the structural changes evidenced in relation to the microstructure of the host material. The Na^+ ion storage in hard carbons involves a combination of edge/defect sites and progresses through adsorption, intercalation and pore-filling, similar to the Li^+ ion storage [62, 63].

As mentioned above, the charge/discharge curves of hard carbon-based anodes in both LIBs and NIBs are featured by a high-voltage sloping region, generally followed by a low-voltage plateau [155]. The former region is often associated with the sodium/lithium intercalation between the disordered layers of the turbostratic nanodomains, while the discharge capacity in the plateau region is ascribed to the

occupation of macropores between turbostratic nanodomains and adsorption into nanopores [53, 63, 153, 156]. The complementary picture has also been proposed, indicating the storage of Na^+ ions in the edges/defects/surface of hard carbons and the turbostratic nanodomain interlayers associated with sloping and plateau regions, respectively [54, 154, 157].

Only a few studies report in *situ* RS analysis in *operando* conditions of hard carbon-based NIBs electrodes. These studies have evidenced that a downshift of the G-band accompanies the increase of capacity in the high-voltage sloping region, while the D-band remains a constant frequency, progressively weakening until it disappears. No further changes in the G-band frequency and D-band intensity are observed in correspondence with the increase of capacity in the plateau region [63, 153]. According to the authors, since the frequency of the G-band is sensitive to the C–C bonding strength, which changes due to the charge transfer from the alkali metal atoms to π^* antibonding orbitals the carbon matrix, its downshift is related to the intercalation process. As the frequency of the G-band no longer varies, as observed in both LIBs and NIBs in the plateau region, no further ions are intercalated. Thus, the downshift gives a measure of the amount of intercalated alkali metal ions, with the different intercalation limits for Li and Na resulting in different minimum frequencies of the G–band. In a simplified picture, an increasing content of alkali metals causes the Fermi level to continuously upshift due to the electron transfer, and the available free states in the conduction band progressively decrease until they are missing. Since the double-resonance process behind the detection of the D-band requires the availability of empty states in the band structure near the Γ-point above the Fermi level, this ultimately leads to the disappearance of the band. Thus, the plateau region capacity is attributed to the pores' surface adsorption and the formation of metal clusters inside them [62].

X-ray absorption spectroscopy (XAS) is able to provide information on the oxidation state, atomic proximity structure, coordination number and bond length of the atoms included in the bulk of a sample [158, 159]. For these reasons, they proved useful in studying the processes of sodiation and de-sodiation at the anode of sodium batteries. A significant drawback of this family of analytical techniques is that it is very challenging to directly probe elements whose atomic number is lower than ca. 20, thus excluding Na and C [160]. Hence, the applicability of XAS techniques is typically limited to anode materials wherein Na species are reversibly stored in phases based on other elements such as Ti [161], Cu [162], Mo [162] and P [163, 164]. Though such anode materials often include a carbonaceous matrix, the latter is introduced mainly to raise the electrical conductivity and not to reverse store Na species. Thus, in most of these anode materials, the carbonaceous matrix does not need the rich morphology and porosity that are bestowed by BCs. Accordingly, conventional artificial carbons are adopted in the synthetic processes (*e.g.*, graphite powder [164], Super C65 carbon [161], reduced graphene oxide [162] or Ketjen black [163]).

Mössbauer spectroscopy is typically used to probe the chemical state of atoms such as Fe [165], Sn [166] and Sb [167], that are often used in carbon-based materials meant for application at the electrodes of electrochemical energy conversion and storage devices [168, 169]. This is particularly relevant if we consider that Sn and Sb are attractive anode materials for sodium-ion batteries due to their remarkable theoretical storage capacities, equal to 847 and 660 mAh g^{-1} [170], respectively. To understand the sodiation/de-sodiation mechanism of materials based on Sn and Sb is of paramount importance to design anodes for sodium-ion batteries exhibiting a maximized capacity and good cyclability [167]. Fe-based anodes for sodium-ion batteries have also been demonstrated and studied with Mössbauer spectroscopy [171]. The literature reports BC anodes, including Sn species [172]. However, such studies are more concerned with elucidating the feasibility of the anodes for application in a sodium-ion battery than with investigating the fundamental sodiation/de-sodiation mechanism of the Sn species. In addition, Mössbauer spectroscopy is of little use for conventional BC anodes for sodium-ion batteries that do not include Sn, Sb and Fe since C is not suitable for the technique [173]. On these bases, the full potential of the Mössbauer spectroscopy in the study of BC anodes for sodium-ion batteries is still to be explored.

Electron paramagnetic resonance (EPR) is an attractive technique for studying BC anodes because it can detect unpaired electrons found in sodium and carbon species [174, 175].. Specifically, it is used effectively to study the BC sodiation/de-sodiation mechanism upon cycling. Na becomes more metallic at the plateau region due to Na intercalation and filling to form clusters, while it is typically ionic at the sloping region [176]. In addition, the metallic sodium clusters are quasi-liquid state at room temperature. Pristine BCs typically do not exhibit EPR signals due to the lack of carbon-centered free radicals and delocalized electrons [176, 177]. However, upon sodiation EPR signals appear, ascribed to SEI films [178] and the formation of metallic bonds similarly to lithium-ion batteries [179]. EPR is particularly suitable also for detecting localized paramagnetic centers associated with different aromatic π radicals on carbon [180]. Such species are strongly affected by the dangling bonds on the carbons [181], which are modulated by the carbon structure and, ultimately, by the pyrolysis temperature. At low pyrolysis temperatures, characteristic localized spin centers are revealed, assigned to dangling σ bonds at sp^2 carbon edges or on open micropores [182]. As the pyrolysis temperature is higher: (i) signals with broad peaks are detected, indicating the presence of conduction carriers; and (ii) it is revealed that few dangling bonds able to react with oxygen are present [183].

Also, electrochemical tools such as Electrochemical Impedance Spectroscopy (EIS) are powerful in determining several relevant features including: (i) the overall ohmic resistance; (ii) the diffusion migration resistance (R_{SEI}) of sodium ions through the SEI film; (iii) the charge transfer resistance

(R_{ct}); (iv) the Warburg impedance (Z_w) associated with the diffusion process of sodium ions inside the material; and (v) the capacitance arising from both the passivation film and the electric double layer capacitor [184]. All these parameters can be determined in *operando* conditions on a fully assembled cell along the charge/discharge process, providing crucial information on the evolution of the anode of the sodium battery upon cycling as the polarization potential is varied [185]. In particular, the diffusion coefficient of sodium in carbon changes between the slope zone and the plateau, indicating a change in the binding energy and a reversible structural phase transition [186, 187]. EIS is also very useful for studying the evolution of the SEI, with a particular reference to its ionic conductivity [174]. EIS parameters determined as a function of the temperature can elucidate the dynamic properties of the resistance and the activation energies for the individual processes or components in the sodium battery. A typical example is the study of the diffusion of sodium ions through the SEI and how the latter phenomenon is affected by the different features of the cell (*e.g.*, the composition of the electrolyte) [188]. A much more detailed picture of the electrical features and of the mechanisms associated with long-range charge transport phenomena can be obtained by broadband electrical spectroscopy (BES) [189-192]. This technique investigates at a high level of detail the electric response of a sample as a function of the frequency of an applied electric field and of the temperature [193]. BES allows for the fine elucidation of the polarization and relaxation phenomena occurring within a material, that are associated with: (i) the mesoscale structure, with a particular reference to the segregation in domains with different permittivity; (ii) the dynamics of the functional groups found within the system. By integrating this information with the outcome of other complimentary techniques (*e.g.*, thermoanalytical analyses carried out by MDSC and DMA [194]; vibrational spectroscopies [195]) it becomes possible to identify the charge percolation pathways and how they are correlated to the composition and physicochemical features of the material. Traditionally, BES has been widely applied to study ion-conducting and cathode materials [196-198]. Very recently, the BES technique has been applied to study the interactions between carbon matrices and electrode materials for battery applications [199]. Specifically, the carbon phase has a primary role in determining the mobility of Li^+ ions in the electroactive material (*e.g.*, $LiCoO_2$) [199]. Though in principle, it is feasible to use BES to investigate battery anodes (*e.g.*, to study intercalation/de-intercalation mechanisms or the features of the SEI), in practice, as of today, very little work has been done in this area. Nevertheless, this leaves the potential of BES to investigate the anodes of sodium batteries based on BCs largely unfulfilled.

Computational modelling can be used to interpret and predict the structure and electrochemical properties of electrode materials for rechargeable batteries, with first-principles density functional theory (DFT) being nowadays the most widely used approach [200, 201]. In this regard, the

electrochemical intercalation of alkali metals in disordered hard carbons or nanoporous carbons remains challenging, mainly due to the structural complexity involved. The structural features of hard carbons, especially the BC produced from biomass, depend on the matrix and the preparation route, and may not be comprehensively captured in simplified models suitable to investigate intercalation phenomena at the atomic scale. The identification of the active sites for the alkali metal uptake needs to be addressed by investigating the structure of hard carbons. Hard carbons typically contain numerous defect sites originating from residual heteroatoms (*i.e.*, hydrogen, oxygen, nitrogen, inorganics), carbon vacancies formed during the heat treatment, and different arrangements of graphitic domains in an otherwise disordered carbon matrix. Thus, the clear relation between structure and electrochemistry behaviour and the dominating mechanisms at the atomic scale for alkali metal insertion/extraction in these systems remains controversial. As already discussed in this section, several interesting mechanisms have been proposed, based on experimental evidence, to interpret the electrochemical structure–property relationships of hard carbon [148, 202], including the "intercalation–adsorption" mechanism, also known as "house of card" model [148], and more recent works that assigned the high-potential sloping region to ion adsorption instead on the defect/edge sites, and the low-potential plateau to ion intercalation into the graphitic layers [203].

Due to this uncertainty, which is critical to be solved to direct the preparation of hard carbons towards optimized microstructures for alkali-ion storage, significant efforts have been devoted in recent years to rationalising the experimental voltage profile from a computational perspective. The main techniques used to this end are DFT-based energy minimization and reactive force field (ReaxFF) molecular dynamics (MD), also in association with Monte Carlo simulations, in the so-called hybrid grand canonical Monte Carlo/MD (GCMC/MD) method [204].

Through computational modelling it is possible to evaluate the feasibility of Na ion intercalation at specific sites by calculating the sodium binding energy according to the following equation (9):

$$E_b = \frac{E_{Bulk+xNa} - E_{Bulk} - x_{Na}E_{Na}}{x_{Na}} \qquad \text{eq. (9)}$$

where $E_{Bulk+xNa}$ is the total energy of the systems with x_{Na} added Na species, E_{Bulk} is the total energy of the systems without Na, x_{Na} is the number of added Na, and E_{Na} is the total energy of one ionic sodium. A positive E_b would indicate that intercalation or storage in the specific system is energetically unfavourable.

Voltage profiles curves, for various model structures, are determined in computational studies from the calculated formation energies of intercalated Na_xC compositions and Na metal (Na_{bcc}), following the equation (10):

$$V(x_2, x_1) = \frac{E(Na_{x2}C_y) - [E(Na_{x1}C_y) + E(Na_{bcc})]}{-zF(x_2 - x_1)} \qquad \text{eq. (10)}$$

where $E(Na_{x1}C_y)$ and $E(Na_{x2}C_y)$ correspond to the formation energies of two structures that differ by the number of Na atoms under a fixed number of carbons, and $E(Na_{bcc})$ is the total energy of metal sodium; F denotes the Faraday constant, z is the number of electrons per Na atom involved in the reaction, and V represent the open-circuit voltage.

While the application of eq. (9) and eq. (10) is straightforward, the real difficulty involved in these calculations is the accuracy in the calculation of the formation energies of intercalated compositions, which strongly depends on the structural model assumed, as well as on the accuracy of the underlying computational approach. DFT-based simulations are expected to give greater accuracy in the calculation of properties related to the electronic structure of HC materials but, due to their computational cost, are limited to relatively small-size models (*i.e.*, 50 atoms [203]), that selectively represent specific structural or defect aspects (*e.g.*, presence of vacancies or oxygen atoms) and the insertion of a very limited number of alkali ions [149, 202, 205-207]. ReaxFF-MD simulations are critical to catch the structural disorder over longer scales, as simulation models can include several thousands of species, thus providing the opportunity to construct models that represent the experimentally observed complex structural features of these systems, including at the same time carbon layers with continuous and irregular curved moieties, different sheet orientation, stack distribution, pore connection, extended defects such as stacking faults and dislocation, expanded layer spacing in graphitic-like domains [208-210].

Energy minimization techniques based on first principle DFT approach have clarified, for example, the reasons behind the different Li/Na/K storage mechanisms of hard carbon anodes, determined by different atomic interactions between the alkali metal and the carbon matrix [206] in graphite-like layers, revealing that much less electrons of Na are transferred in this process compared to Li and K, which indicates the strong Li–C and K–C interactions and a weaker Na–C interaction. In addition, it was found that defects on the carbon layers may have an impact on the atomic interactions including the metal–metal and metal–carbon interactions, thereby determining whether the stored alkali-metal atoms are in ionic or quasi-metallic states.

The application of a combined experimental/computation approach based on DFT modelling of HC supported the proposition of a revised mechanisms of intercalation for Na ions in which the alkali ions are initially bonded simultaneously and continuously at defects, within interlayers and on pore surfaces; subsequently, at higher sodiation level, when such higher energy binding sites are filled, pores filling occurs during the plateau region, where the densely confined sodium takes on a greater degree of metallicity. Based on the structural models investigated, the effect of defects was analysed, suggesting that different defect types influence the energetics of sodium storage differently, both at the defect site and at the nearest sites. In particular, oxygen defects in the graphitic layers were shown

to promote stronger sodium adsorption energies, especially at low sodium loading, which could contribute to the irreversible capacity observed in the first cycle, with sodium remaining trapped at these sites [207].

DFT-based simulations are also used to guide the interpretation of experimental data different from the voltage-capacity profile, such as Raman spectra. For example, using simplified models of graphene layers with AA stacking, the gradual shift of the Raman G-band along with the Na amount inserted between the layers was calculated, in agreement with experiments, while it was suggested that the presence of defects hardly influences the band structure and phonon dispersion. On the contrary, the effect of defects was shown to be significant on the energetics of the systems in terms of voltage profile curves and, in particular, Na diffusion as, for example, migration barriers for Na ions close to defect sites are higher than in regular sites [203].

ReaxFF-MD results can be directly correlated to experimental structural features, such as the interlayer distances, as derived from XRD, the atomic percentages of different carbon components, in terms of sp, sp^2 or sp^3 hybridization, as derived from XPS analysis, and the pair distribution functions (PDFs) to obtain information on the local carbon structure. Such valuable information can not only be used to guide the interpretation of the experimental data but also to assess the validity of the structural model in representing the real structural complexity of the system [208]. Such an assessment is crucial to support the computational findings related to the intercalation mechanism, as this depends upon the HC structure. In particular, based on ReaxFF-MD simulation, the voltage profile curve of HC was interpreted as a three-step process starting with chemisorption on the surface active sites of the graphite sheets, where defects (*e.g.*, non-hexagonal rings) are expected to increase the capacity by promoting the formation of small sodium clusters, followed by intercalation between the carbon layers with suitable d-spacing and, as a final stage, nanopore filling and metal sodium clustering formation.

Few studies explicitly address the computational investigation of biomass-derived HC. In this regard, MD simulations were used, for example, to investigate the alkali ion binding mechanisms and diffusion rates in lignin-based hard carbon models differing by the crystalline volume fraction (CVF) [210]. The hard carbon models were constructed to reproduce the nanostructure of hardwood lignin pyrolyzed and reduced at 1000, 1500, and 2000°C as synthesized and characterized by Tenhaeff et al. [211]. The models included very high numbers of C species (100000-700000 atoms), necessary to capture both the mesoscale structure of lignin-based carbon composite anodes and an accurate CVF with appropriately sized crystallites. Calculation of the binding energy distribution of alkali ions within the C matrix suggests which intercalation positions are more energetically favourable for lithium and sodium, respectively. At the same time, MD simulations are suitable for deriving

diffusion coefficients for the alkali ions in these systems and, consequently, migration barriers for alkali-ion intercalation. Analysis of the results supported a likely intercalation mechanism following the scheme adsorption–intercalation-pore filling sodiation and suggested that lignin-based hard carbons with lower CVF, smaller nanocrystallites, and moderate porosity would allow for the highest energy density for sodiated anodes.

The application of computational-based approaches provides guidance rules to design optimized biomass-derived HC anode materials, notwithstanding the complexity of these systems.

3.2. Use of neat BC as anodic material for NIBs

The first Na-ion cell with BC was assembled in 1993 by Doeff et al. [212], who demonstrated that petroleum coke successfully undergoes reversible insertion of sodium ions and can thus be used in rechargeable NIBs as summarized in Table 2.

Table 2. Overview of neat BC used for the production of NIBs anode materials.

Feedstock	**Pyrolysis conditions**		**Specific Surface Area (m^2/g)**	**d spacing (nm)**	**Highest capacity ($mA\ g^{-1}$)**	**Current density ($mA\ g^{-1}$)**	**ref.**
	Optimal temperature (°C)	**Time (h)**					
Lignin	1300	6	48.3	0.375	183	300	[150]
Olive stones	1400	1	4.1	0.38	291	20	[151]
Saccharides	1300	1	506	0.389	353	25	[213]
Sucrose	1600	2	n.a.	n.a.	270	6000	[51]
Cellulose	1600	1	5	n.a.	310	37	[214]
Banana peels	1100	5	130.8	0.376	355	50	[215]
Coconut shells	1300	1	9	0.391	270	50	[216]
Corn silk	1300	1	6	0.375	273	50	[216]
Walnut shells	1300	1	11	0.368	293	50	[216]
Peat moss	1100	1	196.6	0.37	298	50	[217]
Peanut skin	800	1	1930	0.388	431	100	[218]
Wood	1000	2	n.a.	n.a.	275	10	[219]
Lychee seeds	500	2	6.61	0.37	225	200	[220]
Apple pomace	600	1	117.3	n.a.	255	50	[221]
Apple pomace	600	1	117.3	n.a.	86	5000	[221]
Pine pollen	900	1	171.5	n.a.	201	100	[222]
Hemp haulm	600	3	n.a.	n.a.	256	37.5	[223]
Dandelion	1200	5	4.7	0.37	372	50	[224]
Date palm	1400	1	34.7	0.37	300	25	[225]
Switchgrass	1000	2	619.8	0.376	225	50	[226]
Switchgrass	2050	2	23.1	0.376	110	5000	[226]
Resinous pine wood	1400	1	45	0.381	310	33	[227]

Cellulose nanofibers	1000	2	377	n.a.	255	40	[228]
Bamboo	1000	1	29.1	0.39	320	50	[229]
Cellulose nanocrystals	1000	2	145.6	0.39	340	100	[230]
Lignin/PAN composite	1300	0.5	27	0.373	293	20	[231]
Corn stalks	1000	2	9.24	0.4	270	60	[232]
Maize husks	1100	2	267.7	0.48	255	50	[233]
Reed straw	1300	3	36.2	n.a.	372	25	[234]
Rice husk	1300	2	2.7	0.395	372	25	[235]
Loofah sponge	800	1	n.a.	n.a.	390	25	[236]
Mushroom spores	1400	1	14.7	0.371	303	20	[237]
Argan shells	1200	1	8.6	0.393	333	25	[238]
Peanut shells	600	5	375.2	n.a.	193	250	[239]
Rape seed shucks	700	2	11.9	0.39	196	25	[240]
Rape seed shucks	700	2	11.9	0.39	62	2000	[240]
Lotus stems	1400	1	24.4	0.368	250	100	[241]
Phoenix tree leaves	700	2	1824	0.388	134	100	[242]
Waste tea bag powder	1000	2	521	0.384	193	100	[243]
Waste tea bag powder	1000	2	521	0.384	127	1000	[243]
Algal blooms	1000	5	n.a.	0.365	230	20	[244]
Coffee ground	970	6	787	0.386	173	60	[245]

The use of simple biomolecules such as sugars has been an interesting test bench for the production of hard carbon with tuneable morphologies. As reported by Yamamoto et al. [213], several sugars (*e.g.*, glucose, sucrose, maltose) and sugars based polymers (*e.g.*, cellulose, glycogen, amylopectin) displayed high reversible sodiation capacity, especially thanks to a crucial pyrolytic step at 275°C that stabilizes the carbonaceous structures.

3.2.1. The influence of BC structure on the electrode performances

Li et al. [51] used sucrose for the production of sub-micrometric BC spheres (with an average size of about 300 nm) through a combination of hydrothermal and pyrolytic processes with temperatures ranging from 1000 up to 1600°C. The authors covered the hard carbons with a layer of highly graphitic carbon by mixing the inert carrier gas with toluene vapours. As reported, the initial Coulombic efficiency (CE) of BC spheres reached the 83% and plateau capacity at the low potential region increased with increasing pyrolysis temperature. Accordingly, the BC produced at 1600°C showed a plateau capacity of 220 mAh g^{-1} together with a high cyclability achieving capacity

retention of up to 93% after 100 cycles. The authors also reported full cell characterization using air-stable P2-$Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$ as a cathode, achieving an energy density of 200 Wh kg^{-1} with an initial coulombic efficiency of 76%.

Similarly, Simone et al. [214] pyrolyzed cellulose in a temperature range from 700 up to 1600°C observing a largely graphitic formation for temperatures up to 1150°C. As shown in Figure 7, the authors observed an increment of the plateau and total reversible capacity together with a decrement of slope and irreversible capacity by increasing the pyrolysis temperature.

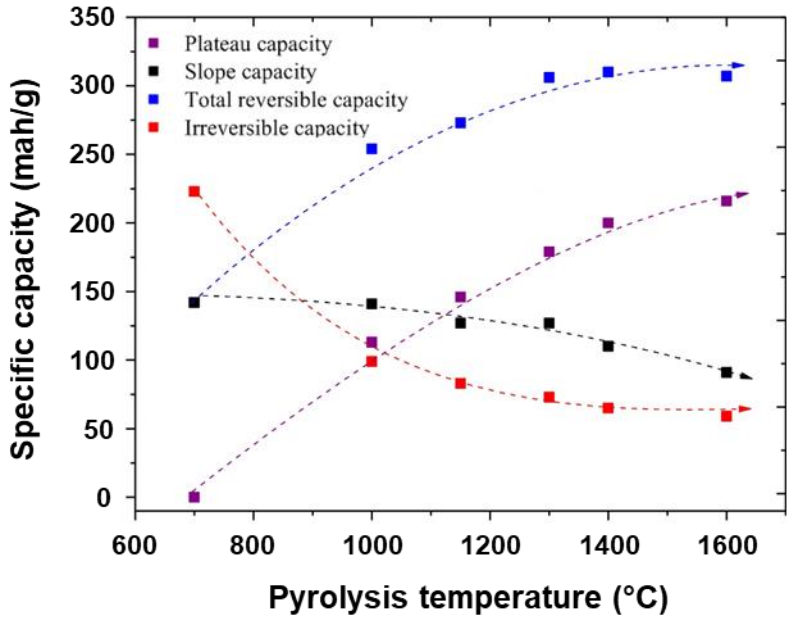

Figure 7: Capacity trends as function of pyrolytic temperature. Reprint with all permission from Simone et al. [214].

Authors suggested that this behaviour was due to a combination of the simultaneous decrement of specific surface area, increment of micropore size and reduction of graphitic plane spacing.

Lotfabad et al. [215] obtained BC converting banana peels reaching a volumetric capacity of about 700 mAh cm^{-3} even with a limited surface area ranging from 19 to 217 m^2 g^{-1}. Nevertheless, the electrodes showed a charge capacity of 221 mAh g^{-1} at 500 mA g^{-1} with a degradation of only 7% after 600 cycles; lower current density (100 mA g^{-1}) resulted in a higher capacity (336 mAh g^{-1}), but with a more pronounced degradation (by 11% after just 300 cycles). Similar values were achieved by Nita et al. [216] by BC derived from coconut shells, walnut shells, and corn silk, all of them with a specific surface area of about 10 m^2 g^{-1}, achieving reversible capacities of around 300 mAh g^{-1} at a current density of 50 mA g^{-1}. Among them, the highest capacity (293 mAh g^{-1}) and the highest capacity retention (93% of the initial capacity after 100 charge/discharge cycles) were reached using walnut shells-derived BC. Authors suggested that the adsorption-insertion mechanism of sodium

storage could be associated with the optimal interlayer space and the presence of defective graphene layers.

Morphological properties of BC are crucial in the activity of BC as anodic material, even more than surface area. Ding et al. [217] converted peat moss into a hierarchical BC with both micro- and meso-porosity in the shape of nanosheets. The porous distribution accounted for the high-rate performance, due to the good accessibility by the electrolyte and the reduced diffusion distances for sodium ions. The authors claimed a very stable cycling capacity of about 298 mAh g^{-1} at a current density of 50 mA g^{-1}, with a CE close to 100% and a negligible voltage hysteresis. Similar results were achieved by producing micro-porous [218] or meso-porous BC [219, 220]. Interestingly, macro-porous materials could also display a remarkably high efficiency. For instance, Fu et al. [221] produced a macro-porous BC (with some tiny pores inside the macropores) derived from apple pomaces, achieving a capacity of 208 mAh g^{-1} with a coulombic efficiency of around 99%. Authors suggested that such a hierarchical 3D structure of BC could provide the microspaces for sodium storage and dissipate the volumetric expansion.

Interconnected 3D networks play a relevant role in BC behaviour in sodium batteries. Zhang et al. [222] produced a honeycomb-structured BC derived from pine pollen, achieving a capacity of 370 mAh g^{-1} at a current density of 0.1 A g^{-1} (the system retained a reversible capacity of 203 mAh g^{-1} after 200 cycles). The authors suggested that the behaviour was due to the large layer spacing among graphitic domains (up to 0.41 nm), favouring sodium ions to intercalation/deintercalation.

Wang et al. [223] moved a step forward and suggested that also the appropriated surface texture could enhance the capacity with an appreciable increment of sodium ions insertion.

Not only the spatial arrangement of the graphitic domains affects the electrode properties, but also the graphitic domains themselves, as proved by Wang et al. [224]. The authors produced dandelion-derived BC using pyrolytic temperatures ranging from 800 to 1400°C, thus increasing the crystallite dimensions from 60 to 210 nm^3. The pyrolytic temperature increase significantly raised the plateau capacity below 0.1 V. However, it did not affect the sloping capacity above 0.1 V, suggesting a strong relationship between the amount of sodium ions deintercalation and the dimension of pseudo-graphitic domains. Similar results were achieved by Izanzar et al. [225] by using date palm waste. Noticeably, BC is a non-graphitizable carbon [36, 246, 247], so the enlargement of graphitic crystallites is limited in space [42], even at high temperatures. Zhang et al. [226] annealed switchgrass derived BC at 2050°C, enlightening interesting features compared with non-annealed BC. Authors reported comparable specific capacities for all pristine and thermally annealed BC by using current density in the range from 0.05 up to 0.1 A g^{-1}, but they pointed out a lower capacity decay for the annealed samples at higher current density (in the range between 0.5 and 5 A g^{-1}). Annealed BC

showed impressive stability with capacity retention of up to 87% over 800 cycles and Coulombic efficiency close to 100%. A very deep insight into the sodium behaviour in BC treated at such high temperatures was reported by Morita et al. [248] by using ^{23}Na-NMR. Authors strongly correlated the size of sodium clusters with the temperature of the annealing process, proving that 2000°C induced the formation of clusters with a quasi-metallic behaviour.

3.2.2. BC electrodes from different feedstocks

The correlation between BC feedstock and its electrochemical performance is complex. Saavedra Rios et al. [249] reported a systematic overview of different feedstocks, such as pine, ash, wheat straw and miscanthus, subjected to the same pyrolytic process at 1400°C. The uncontrolled complexity of the pyrolytic process and the high heterogeneity of the feedstocks in terms of chemical and morphological properties did not allow the definition of a univocal correlation between the used feedstock and the performances of the corresponding electrode. Nevertheless, the authors established a correlation between lignin, hemicellulose and inorganic contents and BC performances, albeit still not fully exhaustive. The study suggested using pure lignocellulosic biomasses BC as a benchmark to evaluate the electrochemical behaviour of the various systems.

Luo et al. [228] used cellulose nanofibers to produce a long-life anode used in rechargeable NIBs. The authors pyrolyzed the feedstock at 1000°C for 2 h, achieving a reversible capacity of 255 mAh g^{-1} at a current density of 40 mA $g^{-1}$and 85 mAh g^{-1} at 2000 mA g^{-1}. The authors observed high cycling stability, with 180 mAh g^{-1} capacity, even after 600 cycles at 200 mA g^{-1}. Similarly, Zhang et al. [229] produced micrometric tubular structures with various lengths but an inner diameter of around 30 nm, reaching a reversible 320 mAh g^{-1} capacity at 5 mA g^{-1}. Alternatively, Zhu et al. [230] pyrolyzed cellulose nanocrystals at 1000°C, producing a porous BC, obtaining a reversible capacity of 340 mAh g^{-1} at a current density of 100 mA g^{-1}.

Jin et al. [231] used lignin to produce nanofibrous BC through a co-pyrolytic process with polyacrylonitrile at temperatures ranging from 800 to 1300°C. The self-standing, binder-free electrode showed a reversible capacity of 293 mAh g^{-1} at a constant current density of 20 mA g^{-1}, with an initial CE of 71%.

Pure lignocellulosic components could be used to produce a wide variety of BC architectures. However, their isolation from biomasses requires multistep processes that make them not so appealing; as a matter of fact, lignocellulose is usually used as a whole for the production of anode material. One of the most abundant and economically convenient sources of lignocellulose is crop-derived biomass, even if its use represents an ethical issue due to food destination [250]. Many studies have exploited the use of crop residues and derivatives as the source for the production of BC to be

used in energy devices. Cong et al. [232] hydrothermally treated corn stalks, simultaneously carbonizing the biomass and removing the inorganic components. The so-obtained material was used without further treatments as an anodic material, with a reversible capacity of 270 mAh g^{-1} at 0.2 C and 172 mAh g^{-1} at 10C (the capacity was remarkably maintained up to 97% of the initial one even after 100 cycles).

Yang et al. [233] studied BC obtained from pyrolyzed maize at different temperatures from 500 up to 1100°C. BC produced at 500°C did not display any electrochemical activity, while the other samples were conductive enough to be used as electrode material. Authors reported the best performances using BC produced at 1100°C, achieving a reversible 240 mAh g^{-1} capacity. Also, rice derived waste-streams [234, 235] and old loofah sponges [236] are good choices to produce anode for NIBs, with specific capacities above 350 mAh g^{-1} at 25 mA g^{-1}current density.

Several other neat lignocellulosic biomasses (*i.e.*, mushroom spores [237], argan shells [238], peat moss [217], peanut shell [239], rape seed shuck [240], lotus [241], leaves [236, 242]) have been used to produce BC for NIBs applications. However, using biomass waste-streams represents a very interesting route to improve the BC-based electrodes sustainability. Arie et al. [243] used waste tea bags derived BC as feedstock for a hydrothermal/pyrolytic conversion route producing NIBs anodes with an initial capacity of 375 mAh g^{-1} at a current density of 100 mA g^{-1}, maintaining a capacity of 193 mAh g^{-1} after 100 cycles.

Another interesting approach is based on the conversion of harmful biomasses, such as those recovered from algal blooms, as reported by Meng et al. [244]. The authors pyrolyzed the feedstock in a temperature range from 700 up to 1000°C, achieving a specific capacity of 230 mAh g^{-1} at a current density of 20 mA g^{-1}.

3.3. Use of engineered BC as anodic materials for NIBs

Tailoring the chemical properties of BC (by following some of the strategies described in Section 2.2) is a key issue for adjusting its performances as an anodic material, as overviewed in Table 3.

Table 3. Overview of engineered BC used for the production of NIBs anodic materials.

Biomass feedstock	Functionality insert	Tailoring reactant	Surface Area (m^2/g)	Specific capacity (mAh g^{-1})	Capacity of not doped BC (mAh g^{-1})	Current density (mA g^{-1})	ref.
Wood powder	C=O	Tetramethoxysilane	n.a.	330	190	40	[251]
Grapefruit peels	N	Melamine, urea and citric acid	10	187	110	37	[252]
Cellulose	N	Chitosan	n.a.	395	278	100	[253]
Okara from soybean	N	Main feedstock	n.a.	292	/	56	[254]
Honey	N	Main feedstock	677	394	/	100	[255]

Algae-Carrageen	S, N, O	Main feedstock	852	109	/	10000	[256]
Waste bagasse	S, N	Melamine (N) and sulfur powder (S)	110	745	200	100	[257]
Leaves	P	Phosphoric acid	601	310	90	100	[258]
Carrageenan fibers	FeS_2	$FeCl_3$ ethanol solution	265	283	75	1000	[259]
Brown seaweeds	FeS	$FeCl_3$ aqueous solution	60	385	/	2000	[260]
Carrageenan fibers	Ni_3S_4	$NiCl_2$ ethanol solution	485	297	/	1000	[261]
Coir pith	Sb_2S_3	$SbCl_3$ and cysteine	1560	443	288	100	[262]
Coir pith	Sb_2S_3	$SbCl_3$ and cysteine	1560	208	117	2000	[262]
Chlorella	MoS_2	Phosphomolybdic acid	n.a.	175	70	5000	[263]
Chlorella	MoS_2	Phosphomolybdic acid	n.a.	413	135	50	[263]
Chlorella	MoS_2, Sn	Phosphomolybdic acid, $SnSO_4$	n.a.	167	/	15000	[264]
Popcorn	MoS_2	Aqueous solution of ammonium heptamolybdate ($(NH_4)6Mo_7O_{24}$)	n.a.	406.9	80	200	[265]
Black fungus	Sb_2O_4	$SbCl_3$	2233	567	/	100	[266]
Blackberry seed	Sb_2O_4	$SbCl_3$	22	935	236	100	[267]
Mangosteen epicarp	$MoSe_2$	Na_2MoO_4 in ethanol, selenium in N_2H_4	289	405	108	200	[268]

A first feasible approach is the pre-treatment of the feedstock to remove the inorganic content. Beda et al. [269] studied three different cellulose-rich biomasses (*i.e.*, asparagus, potato and grape waste), either washing the biomass with water at 60°C before the pyrolysis or washing the pyrolyzed BC with hydrochloric acid at room temperature. These two gentle wash procedures reduced the inorganic content of about 10 wt.% on the final BC (with respect to the BC obtained without any washing treatment). Interestingly, the BC produced by both routes showed slightly higher surface area values than non-treated BC, in the 50 $m^2 g^{-1}$ range. Nevertheless, the electrochemical capacity of the washed materials is not significantly higher than the capacity of non-washed BC (only when the washing step is carried out before the pyrolysis, the capacity is slightly higher). Susanti et al. achieved a more effective demineralization using hydrochloric acid on BC at 60°C for 24h [270]. The resulting BC showed improved performances compared with the neat one, showing high capacity at a current density of 50 mA g^{-1} (up to 317 mAh g^{-1} at the beginning, with a plateau capacity at 244 mAh g^{-1} after several cycles). Interestingly, the authors reported that the demineralization of the feedstock with potassium hydroxide before the pyrolysis, instead, does not significantly affect the electrochemical activity of the material. These observations suggested that pre-treatments induced different reorganizations of the biomass before the pyrolytic conversions, acting not only on inorganic content but also on organic components. This emerged from the work of Dou et al. [271], which proved the detrimental effect of strong and prolonged acidic pre-treatment on the electrochemical performances of the resulting BC. On the other hand, Feng et al. [272] proved that a controlled pre-

hydrolytic step mediated by enzymes could boost the properties of the produced BC: indeed, the removal of hemicellulose component increased the amount of pseudo-graphitic domains with a great interlayer spacing, appreciably improving the specific capacity.

Acid treatments could also be used to functionalize and activate the BC. Hong et al. reported that a biomass pre-treatment with phosphoric acid could lead to a very high surface area BC (up to 1272 m^2 g^{-1}), functionalized with phosphoric residues [273]. This material showed a capacity of 181 mAh g^{-1} at a current density of 200 mA g^{-1} (even after 200 cycles), but a very poor CE of about 27% was obtained due to the formation of solid electrolyte interphase induced by phosphorus residues.

Another route for chemical activation was studied by Li et al. [274] by using potassium hydroxide on a cucumber stem-derived BC. The authors followed a two-step process, starting with the pyrolysis at 1000°C followed by a hydrothermal activation step at 150°C with a water solution of KOH. Activated BC showed an improvement in the reversible capacity by 36% with respect to the pristine one.

Another non-acid chemical activation route was reported by Sahu et al. [275] using calcium hypochlorite and activation temperatures ranging from 400 to 900°C, producing the materials displayed in Figure 8.

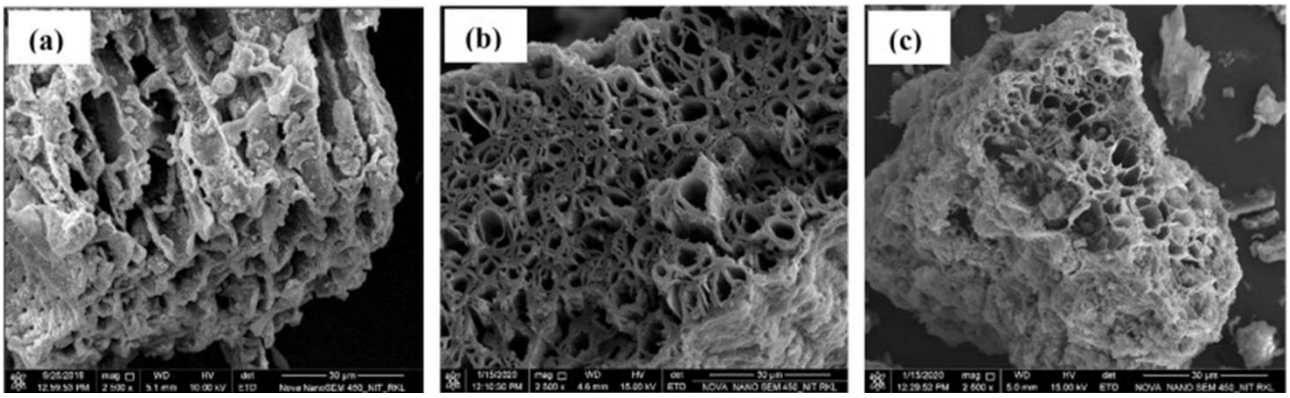

Figure 8: Scanning electron microscope images of activated BC produced at (a) 400°C, (b) 600°C and (c) 900°C, as reported in ref. [275]. Reprinted with all permissions from Elsevier.

The partial oxidation promoted by $Ca(ClO)_2$ induced the conversion of the more amorphous domains of BC into carbon dioxide (in the same way as many other common oxidant agents, such as nitric acid). The *in situ* released carbon dioxide could also act as an activation agent itself, as mentioned in the previous section. The activated BC shown in Figure 8 presents a lamellae-like surface, with the simultaneous disappearance of the micrometric porosity. Authors suggested without reporting any electrochemical test that the high porous volume (up to 0.141 g cm^{-3}) together with the improvement of graphitization and surface area, could make this BC suitable for sodium ions storage.

Very recently, also dos Reis et al. demonstrated the importance of increasing the porosity to increase the capacity: by treating BC with $ZnCl_2$, they induced the formation of ordered mesopores almost doubling the specific capacity with respect to the untreated material [276].

The activation process acts not merely on surface area and porous volume and distribution, but also on heteroatom doping of the carbonaceous matrix of BC. Heteroatom doping is an effective route for enhancing the BC activity as anodic materials for NIBs. Chen et al. [251] doped a woody-derived BC by co-pyrolyzing the feedstock together with tetramethoxysilane. The tailored BC was functionalized with abundant carbonyl residue that enlarged the quasi-graphitic domains improving the Na^+ storage process. Similarly, nitrogen doping is generally achieved by using organic species that undergo to radical decomposition with the formation of highly reactive nitrogen-based radicals able to tailor the BC surface.

Romero-Cano et al. [252] used a mixture of melamine, urea and citric acid to produce a nitrogen-doped grapefruit peel-derived BC. The presence of nitrogen sites induced a more efficient sodium transport inside the pores and increased the BC disorder, leading to a stable sodium intercalation capacity of 180 mAh g^{-1} at a current density of 40 mA g^{-1}.

Alternatively, the co-pyrolysis of lignocellulosic biomass with nitrogen-rich biopolymers (such as chitosan) is a reliable route to produce nitrogen-containing BC. Enforcing this approach, Dan et al. [253] pyrolyzed a mixture of cellulose and chitosan for the production of a hybrid material composed of nitrogen-doped BC and graphene oxide, with a remarkable capacity of 227 mAh g^{-1} at 5000 mA g^{-1}. Similar results were achieved by the pyrolytic conversion of protein-rich feedstocks, such as okara [254] and honey [255]. Some authors also report the beneficial effect of sulphur [256, 257] and phosphorous [258] doping, which reduces the irreversible Na^+ trapping.

Another broadly investigated strategy to tailor BC properties is the introduction of inorganic species. A clear example is represented by metal sulphide particles supported onto BC. These materials are promising as anodes for NIBs due to their high theoretical capacities, but their use is slowed down due to their poor electronic conductivity and low structural stability during the charge/discharge process. Many examples are reported in literature, based on different metal sulphides: iron [259, 260], nickel [261], antimony [262] and molybdenum [263-265], deposited either as a sulphide layer or as sulphide nanoparticles onto BC surface. Similar results were achieved by depositing antimony oxides [266, 267] and molybdenum and tungsten selenides [268, 277].

A different approach was reported by Wang et al. [278], mixing the biomass directly with a nickel catalyst prior to the pyrolytic process to tailor the morphology of the produced particles and enhance the graphitization degree. The BC obtained using the Ni catalyst evidenced an increase of the initial

CE by 40%. Moreover, the authors evidenced the formation of thinner solid electrolyte interphase, thus reducing the charge transfer resistance and increasing the reversible capacity.

Finally, physical activation is also a well-established route for improving the electrochemical performances of BC. Kumaresan et al. [156] reported a BC obtained from pyrolyzed flower-derived feedstock and physically activated in a controlled carbon dioxide atmosphere. The authors reported an improvement of initial capacity by 10% after activation at 1400°C with respect to the same BC not activated, achieving a capacity of 413 mAh g^{-1}. They correlated the enhanced activity to the introduction of defective edges on graphitic domains, with an increased disorder in their arrangement and the formation of new micropores.

3.4 The relationship between BC physiochemical and electrochemical properties: a small conundrum

The production and engineering of BC is matter of great complexity due the simultaneous influence of multiple factors ranging from the raw materials to the pyrolytic conditions (i.e. temperature, heating rate, reactor geometry), together with possible post processing routes including activation and tailoring process. Depending on these processes, BC can be obtained with different structural and morphological properties, such as the specific surface area and the d-spacing among the graphitic layers, both properties affecting the electrochemical behaviour of BC. Figure 9a allows graphically visualizing the results reported in Table 2, where all the tested BC materials displayed a d-spacing above 0.37 nm (that is higher than the graphite d-spacing of 0.34 nm and necessary for Na^+ intercalation/deintercalation [62], but a clear trend between the values of d-spacing and the obtained electrochemical capacity cannot be defined; on the other side, the highest capacity was obtained with a BC material with a very high surface area (1930 m^2/g, [279]), although some remarkable results were reported even in cases of specific surface area lower than 200 m^2/g. As a guideline for further works in this field, Figure 9b shows the dependency of the capacities reported in Table 2 with respect to the pyrolysis temperature (that represents a way to control the graphitization degree) and to the specific surface area (that is easily tuned by means of all the surface tailoring procedures described in Section 2.2). In this respect, the positive effect of increasing the pyrolysis temperature emerges, even more pronounced than the effect of the specific surface area (considering that, for instance, there are at least three reported records in which the area is higher than 500 m^2/g but the capacity is lower than 200 mAh/g, [226, 242, 243].

Data set reported in Figure 9 provide just a general overview and not a strict regulation, since they are put together results obtained by different research groups on BC materials prepared from different raw materials and tested in different conditions in terms of electrochemical cells, electrodes formulations, combined electrolytes, and electric current densities. NIBs anode materials do not involve only pure BC, but many studies have been devoted to the preparation of doped materials with

enhanced performances, as summarized in Table 3. In particular, the presence of both heteroatoms included into the carbon structure (mainly N, O, and S) and of inorganic compounds finely dispersed within the matrix was exploited to increase the capacity of poorly performing BC materials (even at very high current rates) [251, 256, 257, 259, 260, 262-265, 267].

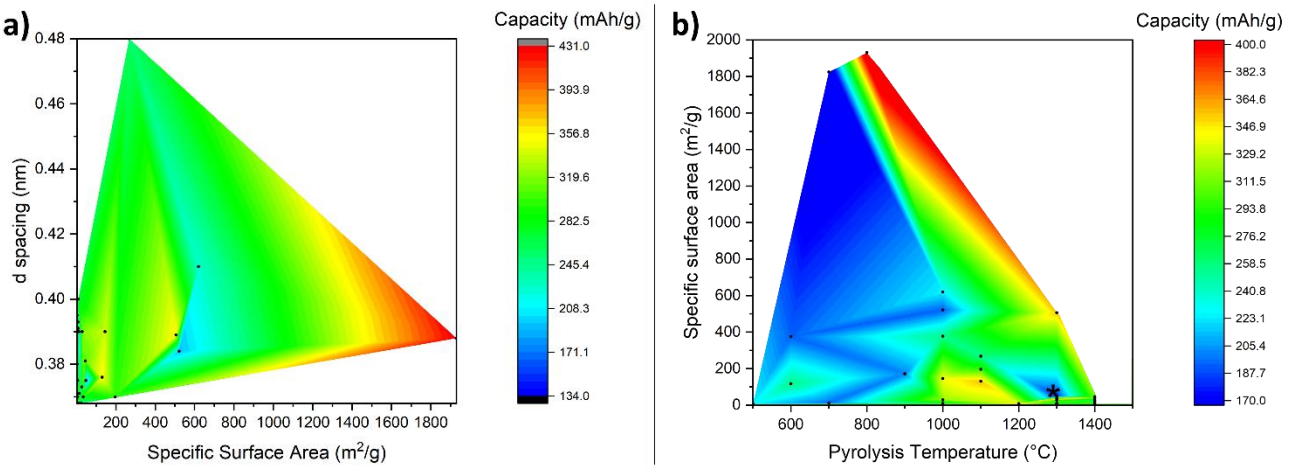

Figure 9: a) Relationship between the highest capacity of BC in NIBs and the structural properties in terms of specific surface area and d-spacing among the graphitic layers (not all the literature references report the values of those structural parameters). b) Dependency of the capacity with respect to controlled parameters as pyrolysis temperature and specific surface area (*this datum is out of trend because the cell was tested at much higher current density as a proof of concept for fast charge/discharge applications). Data adapted from Table 2 and related references.

4. Beyond NIBs: a perspective on the use of BC as electrode material in other post-Li batteries

The use of BCs as electrodes for post-lithium batteries is not limited to sodium-ion batteries. Their outstanding microstructural and electrochemical properties, which have already been discussed above, allow for the insertion of other monovalent ions (namely K^+) at low potential [280], thus making them suitable as anode materials. Moreover, their electrochemical stability towards oxidation, the electronic conductivity and the surface chemistry (*i.e.*, presence of functional groups) open up ways towards their use as positive electrodes for Metal-Sulphur and Metal-Air batteries[281].

4.1 BC as anode material for K-ion batteries

With its very low standard reduction potential (-2.936 V vs SHE) and smaller solvation shell compared to that of lithium and sodium ions in most electrolytes [282], as well as high abundance on Earth's crust (1.5 wt.% of potassium compared to the total mass of the crust) [279], Potassium-ion

batteries (KIBs) are nowadays considered another interesting candidate as an alternative to LIBs. Unlike Na^+, K^+ can reversibly intercalate between graphite layers with a theoretical capacity of 273 mAh g^{-1}, but generally, the huge volume change that occurs during intercalation/extraction compromises the Coulombic efficiency and stability [283].

Due to K^+ ion elevated ionic radii, an efficient and stable KIB anode must be tailored to buffer the volume changes produced by K^+ movement inside and outside the structure. Biomass-derived carbons present a considerable variety of morphologies and microstructures, which can be tuned to fit the requirements for efficient potassium intercalation/extraction [284, 285]. Those features are generally brought by a highly ordered degree of local structure but a rather disrupted order in the long-range [286]. For example, Zhang et al. [287] modelled the Von Mises stress distribution induced by K^+ insertion/extraction on different shaped-carbons: solid spheres, hollow spheres, hollow bowls and hollow multihole bowls, accompanying the obtained theoretical data with experimental investigations on different biomass-derived carbons. They showed that the more open the structure, the lower the stress produced by potassium insertion, identifying hollow multihole bowls as the best option. This result was confirmed by experimental analyses, where their best sample, BC-derived multihole bowls obtained via a hydrothermal synthesis followed by physical and then chemical activation, was able to reach capacities of 304 mAh g^{-1} after 150 cycles at a current density of 0.1 A g^{-1}, among the highest specific capacities recorded for KIB anodes.

BC composition is another critical factor that can improve the storage properties of potassium cells. Most BCs display a heteroatom-doping which is the legacy of the original biological sample's composition (intrinsic doping), but which can also be introduced during the synthetic steps (extrinsic doping) [8]. As already stated, heteroatoms positioned in place of carbon can change the local structure of the carbonaceous matrix, thus forming active sites that can electrochemically react with alkali-ions but also changing the structure of the BC itself. Recently, Lu et al. [288] proposed a pinecone-derived N-doped BC with a porous pie-like structure as anode material for KIBs. Such char was synthesized via a chemical activation reaction with molten $ZnCl_2$ and urea as nitrogen source, followed by cleaning steps. The N-doped BC was able to deliver a capacity of 267 mAh g^{-1} after 100 cycles at 50 mA g^{-1}, almost two times that obtained with the same char without N-doping. Also, the nitrogen-doped carbon was able to achieve 109 mAh g^{-1} after 1000 cycles at 5 A g^{-1}, further proving the benefits of doping. The authors also state that the activation process using $ZnCl_2$ as molten salt can work synergistically with the doping by forming a meso- and macroporous structure suitable for potassium insertion.

Several authors have also used co-doping of BCs with multiple heteroatoms to tune their properties to fit KIBs requirements. A recent example is that of Yang et al. [289], which synthesized a nitrogen,

oxygen and phosphorus co-doped biomass-derived carbon as anode for potassium-ion batteries. The BC, derived from sessile puffballs, was prepared by reaction of the carbon source with diethylenetriamine and tributyl phosphate in a polytetrafluoroethylene liner at 200 degrees, followed by the pyrolysis in nitrogen atmosphere. The obtained NOP-BC showed a mesoporous hollow spherical structure with excellent electrochemical properties, such as a high specific capacity of 352 mAh g^{-1} after 600 cycles at 200 mA g^{-1} with a CE of about 97.5%. Once again, the presence of voids inside the BC structure provides an ideal condition to accommodate K^+ without stressing too much the structure.

4.2 BC as cathodes for Lithium-Sulphur batteries

Another important contender for the throne held by LIBs in the global market is that of Lithium-Sulphur (Li-S) batteries. Elemental sulphur can be electrochemically lithiated at a potential of 2.1 V, with a theoretical specific capacity of 1672 mAh g^{-1}, for an overall gravimetric energy density of 2552 Wh g^{-1}, almost one order of magnitude higher than conventional LIBs [290]. Unfortunately, such a reaction brings to the formation of the well-known polysulfides that, being soluble in most of the electrolytes used in Li-S batteries, bring to the rapid capacity decay of the battery. The polysulphide solubility and the sulphur low electric conductivity make its incorporation in conductive matrixes necessary to mitigate the polysulphide solubilization and guarantee an efficient electronic percolation through the electrode [291]. Biomass-derived carbon can be successfully employed in this field because it has strong physical and chemical adsorption properties towards polysulphides and high electric conductivity [292, 293].

Pore size and surface area are among the most important parameters that define a good carbon matrix for Li-S cathodes. Generally, a high specific surface area translates into more space for sulphur to fit into [294], but it has little effect on polysulfide dissolution. The dimension of pores is, in fact, crucial: micropores (pore width < 2 nm) have been proven to be suitable for polysulphides adsorption [295], while larger pores (width from 2 to 50 nm) are good for sulphur encapsulation [296]. An example is the work of Yang et al.[297], where a biomass-based carbon with both the aforementioned porosities was synthesized and tested as a cathode for Li-S batteries. Such BC was synthesised starting from garlic acid, a natural phenolic component of several plants, via a chemical activation involving a surfactant and zinc acetate. The resulting product presented both small (< 5 nm) and big (> 10 nm) pores and was able to operate with an initial reversible capacity of more than 800 mAh g^{-1} at 0.1C and a retention of more than 80% after 200 cycles at 0.5C. This is due to the presence of both kinds of porosity, simultaneously able to encapsulate a good amount of sulphur (1.6 mg cm^{-2}) and to delay polysulfides dissolution.

Once again, doping the BC with heteroatoms can be beneficial for several reasons. One of them, which is shared with KIBs, is the improvement of conductivity, which is particularly important in Li-S batteries, due to the low electronic conductivity of sulphur. As already stated, this can be achieved via N-doping, which has the second advantage of creating a positively polarized defect with excellent adsorption properties towards the negative polysulfide ions [292, 298]. As for KIBs applications, co-doping with BC with nitrogen, sulphur [299, 300] and phosphorus [301] can be used to tune the char's properties, in this case, to encapsulate better and adsorb the polysulfides. Despite all the advantages brought by such defects, their interaction with the polysulfides remains characterized by weak Van der Waals interactions [302]. In order to hinder the polysulfides diffusion and migration even further, an interesting strategy is introducing metallic compounds in the BC /sulphur cathode to have sites in which the polysulphides can chemisorb [303-305]. A recent and explicative example of this approach is that of Lin et al.[306], who synthesized a biomass-derived N, S, P co-doped carbon (soybean sprouts' stems as a precursor) and then coated such char with a layer of nitrogen-doped carbon dotted with CoSe nanoparticles. When embedded with sulphur, such compound achieved an excellent capacity of 796 mAh g^{-1} at a current as high as 4C, then reduced to 420 mAh g^{-1} after 700 cycles. Even at a low current of 0.2C, the capacity fading per cycle was about 0.04%, which is to be considered a small value for LSBs.

4.3 BC as cathodes for Metal-Air batteries

The versatility of BC makes them attractive for yet another post-lithium technology: that of metal-air batteries, among which Li-O_2 is the most famous and studied. Such devices rely on the electrochemical reaction between oxygen and metal for a theoretical energy density of 3458 Wh kg^{-1} for Li-O_2 ones. In this case, a good cathode material should be able to promote the oxygen reduction reaction [307] but also its evolution, which is generally hindered by the formation of insoluble discharge products (Li_2O_2 in the case of Li-O_2 batteries), which risk blocking the pathways of O_2 and electrolytes [281, 308]. Once again, heteroatom-doped BC has been proposed for this role and used in devices like Li-Air [309], Al-Air [310, 311] and Zn-Air [312, 313] batteries. The presence of metal compounds in carbon matrices can further improve the electrocatalytic activity of metal-air cathodes [314-316]. A recent example has been reported by Jing et al., who developed a BC co-doped with nitrogen and cobalt as cathodes for Li-O_2 batteries [317]. Such BC, synthesized from paulownia wood via pyrolysis in the presence of melamine and $CoCl_2$ as nitrogen and cobalt sources, showed 3D channels with pore sizes ranging from micro to macropores suitable for oxygen permeation. The obtained self-standing electrode was directly used as a cathode in a Li-Air battery, showing a specific capacity as high as 9 mAh cm^{-2} at 0.05 mA cm^{-2} and excellent cyclic stability at higher currents.

5. Considerations about NIBs sustainability and the role of BC

Energy storage is an unneglectable part of daily life, granting the functioning and integrity of a wide range of industrial ecosystems and infrastructures. The development of lithium-based batteries revolutionized the way to face the energy storage world [318]. Nevertheless, lithium has rapidly become a critical raw material, and its use has fed a high environmental impacting economy [4]. NIBs are among the most suitable candidate to replace lithium-based technology, but their environmental impact is more complex than could appear by a simple look. As Schneider et al. reported [319], greenhouse gas (GHS) normalized on the specific energy emitted by assembling a NIB is sensibly higher compared with a LIB that showed more favourable life cycle assessment outputs. This consideration enlightens one of the challenges of the NIBs field: the need to increase the performances. BC could play a relevant role in the decrement of GHG emissions associated with NIBs development. As reported by Kane et al. [320], the replacement of carbon black with BC for anode production reduced the CO_2 emission by up to around 50 %. Establishing a high-value application such as NIBs production could spread BC productive sites. The lack of consolidated producers is a main drawback in the BC-based economy [321]. NIBs growth could represent the change to exploit the BC in a strategic field promoting the development of a virtuous economic model that could be established in both developed [322, 323] and undeveloped countries [324, 325]. Nevertheless, the real impact of BC on the GHS decrement is matter of great complexity. As reported by Matuštík et al. [326], the environmental impact of BC is strictly related to the socio-economic environment which surround the production platforms including both technological and logistic issues. The main problem related to the BC sustainable production is the choice between small pyrolytic units able to operate on demand and industrial scale plant that required biomass transportation on site from abroad[327]. The balance between the fuel used for biomass transportation to big plant[327] and poor efficiency of a small units[328, 329] is the great conundrum of the BC production and it still debate. The energetic infrastructure plays a great role on GHS produced during the BC production and a fully based renewable energetic source should be employed for significantly decreased the GHS emissions[327]. This complex scenario should be carefully considered and the best solution should be implemented considering all the aspect of BC and BC based materials.

6. Conclusions and suggestions for future research

Electrochemical energy storage devices having enhanced energy and power densities are nowadays utterly important for the intermittent storage of renewable energy, thus reducing the dependency from fossil fuels, and fighting climate changes. Nevertheless, some critical point regarding both materials availability and technology readiness should be faced for implanting a virtuous paradigm shift of

energetic market. The scarcity of critical materials represent the first relevant issue for now and the near future. As an example, the European Commission classified natural graphite as a critical raw material (CRM) and battery-grade natural graphite as a strategic raw material; actually, graphite has also been recognized as a CRM by Japan, Canada and the US. Thanks to many appealing features, including abundance, low cost, conductivity, reversible intercalation of sodium ion at low potential, and easiness in tailoring over its intrinsic properties, BC, the solid carbonaceous material obtained from pyrolysis of biomass waste, stands as a promising active material for developing efficient Na-ion batteries. The bio-derived, ubiquitous, renewable nature of BC, and the possibility of including its production into integrated biorefinery platforms could represent a real game changer for NIBs, one of the technologies of choice, not only to mitigate the environmental concern, but also to promote the development of sustainable energy storage applications.

Recently, there has been considerable interest about solid carbon enriched materials produced via different thermochemical techniques such as pyrolysis, however there are still obstacles to overcome towards the proper exploitation of these auspicious materials in real operational devices. Albeit they are obtained as added-value products from waste, thus in principle costless, precursors, their synthesis is still not too advantageous from the economic/environmental viewpoint compared to the simple biomass waste disposal. Hence, novel and greener synthesis routes and production procedures have to be developed and optimized in view of upscaling acceleration and truly sustainable mass market deployment, paying particular attention to upgrading the processing technologies to maximize biomass-based materials utilization with high efficiency, low cost and improved added value. It is also widely assumed that more in depth analysis over the acting mechanisms of activators/dopants and knowledge over controlling and tailoring the pore geometry and interlayer carbon spacing are still necessary; indeed, unravelling the correlation between biomass precursors features/composition and resulting BC active material properties in terms of desirable nano-/micro-structural characteristics is fundamental to achieve higher energy density anode materials.

Here, we have summarized and discussed the most recent progresses towards the conversion and efficient utilization of biomass and its derived biochar as NIB negative electrode materials. The effects of various parameters involved in the synthesis methods to tailor morphology, surface area, pore structure, and composition of BC, together with the structure-activity relationships towards the development of high performing electrodes and devices have been elaborated, evidencing the possible, relevant future role of efficiently utilizing biomass and its derived biochar towards realizing sustainable energy storage devices. Many approaches are proposed in the literature to finely tune the BC properties, from the choice of the proper biomass feedstock to the pre- and post-production tailoring processes. The complexity of relationship between BC features and electrochemical

performances is elusive, but it emerged the key role of post-production modifications for boosting BC performance.

Similarly, Na-ion batteries are still some steps away from production and commercialization on a large-scale, BC-based NIBs stand as one of the candidates to lead the transition to a new energy economy paradigm. Several challenges remain and the proper linkage between the BC production and biomass waste utilization plays a vital role in reducing the amount of waste being thrown and discarded by, for instance, agricultural, landfill, and sewage sectors into more valuable products, while concurrently designing high-performance and fully bio-derived energy storage devices and helping in lowering pollution. In this respect, the present review is expected to inspire additional future research into the smart production of BC from biomass waste and its application as high added value active material in next generation batteries.

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