Structure and function of hard carbon negative electrodes for sodium-ion batteries

Uttam Mittal, Lisa Djuandhi, Neeraj Sharma and Henrik L Andersen

1 School of Chemistry, University of New South Wales, Sydney, NSW, 2052, Australia
2 Departamento de Física de Materiales, Universidad Complutense de Madrid, 28040 Madrid, Spain
* Authors to whom any correspondence should be addressed.
E-mail: uttam.mittal@unsw.edu.au and henrikla@ucm.es

Keywords: hard carbons, anodes, characterisation techniques, alkali-ion batteries, Na-ion batteries

Abstract

Practical utilisation of renewable energy from intermittent sustainable sources such as solar and wind relies on safe, reliable, cost-effective, and high-capacity energy storage systems to be incorporated into the grid. Among the most promising technologies aimed towards this application are sodium-ion batteries (SIBs). Currently, hard carbon is the leading negative electrode material for SIBs given its relatively good electrochemical performance and low cost. Furthermore, hard carbon can be produced from a diverse range of readily available waste and renewable biomass sources making this an ideal material for the circular economy. In facilitating future developments on the use of hard carbon-based electrode materials for SIBs, this review curates several analytical techniques that have been useful in providing structure-property insight and stresses the need for overall assessment to be based on a combination of complementary techniques. It also emphasises several key challenges in the characterisation of hard carbons and how various in situ and operando techniques can help unravel those challenges by providing us with a better understanding of these systems during operation thereby allowing us to design high-performance hard carbon materials for next-generation batteries.

1. Introduction

In recent years, there has been an accelerating adoption of renewable energy around the world due to the environmental benefits as well as supply issues associated with the utilisation of non-renewable resources (e.g. petroleum, coal, and natural gas). However, when integrated into the existing electrical grid systems, the intermittent nature of e.g. solar and wind energy generation is likely to cause grid instability [1]. As a result, the widespread integration/adoption of energy from renewable resources relies on low-cost, scalable, and stable storage systems [2]. In this context, electrochemical energy storage in battery systems is among the leading technologies for providing the large-scale energy storage capacity necessary to facilitate the transition from fossil-fuel-based energy to renewable energy [3]. Despite the obvious benefits associated with existing Li-ion battery (LIB) technologies in terms of energy density, sodium-ion batteries (SIBs) are emerging as a more viable contender for large-scale stationary energy storage. This is mainly because SIBs feature a lower cost of input materials for fabrication relative to LIBs, thereby enabling total energy capabilities similar to LIBs to be achieved at a much lower price per kilowatt hour [4]. Additionally, SIBs are considered more environmentally friendly due to aspects such as potentially Co/Ni-free electrodes and their more facile recyclability enabled by the possibility of using Al as the current collector for both anode and cathode. The latter also generates a lower-cost battery [5]. As such, SIB energy storage systems are being commercially introduced into the market by Contemporary Amperex Technology Co Ltd [6] and organisations such as AMTE Power, Faradion, and Reliance Industries are also making significant inroads into this space [7]. However, several challenges remain unsolved including the optimisation of both cathode and anode materials capable of reversible insertion and extraction of sodium ions.
Graphitic carbon has effectively been the uncontested anode material of choice in LIBs for more than 30 years [8, 9], but the implementation of graphite anodes into SIBs has so far been unsuccessful [10]. It is incorrectly assumed that there is an inherent incompatibility between the graphite interlayer distance and the Na\(^+\)-ionic radius, which prevents Na\(^+\) intercalation into graphite [11]. However, it is due to the thermodynamic instability of the binary Na-intercalated graphite intercalation compounds [12]. Interestingly, experimental observations of Na-intercalation (often co-intercalation) into graphitic regions have been demonstrated using sodium triflate in diglyme electrolyte [13, 14] as well as ether-based electrolytes [12, 15, 16] producing high rate capability and coulombic efficiency. As such, the scope to harness Na intercalation into graphite in SIBs has not been completely ruled out [17], but issues faced include large volumetric expansion in the range of 200%–300% for [Na-ether\(^+\)] intercalation [12], the relatively high redox potential of around 0.6–0.8 V vs. Na\(^+\)/Na [18], the low energy density in full cells [19], and a general lack of mechanistic understanding [13]. Consequently, non-graphitic carbonaceous materials such as soft and particularly hard carbons are currently the leading anode materials for the SIB systems due to their relatively low cost, high accessibility, sustainability, facile synthesis, and superior electrochemical stability [20–30]. The development of hard carbon anode materials is in part restricted by our limited understanding of the fundamental structural mechanisms at play within the materials during operation. In order to improve the performance, a detailed understanding of the relationship between their structure, structural dynamics, and electrochemical properties is required. These components of SIBs and their operational parameters possess different specifications and requirements in characterisation and thus obtaining the necessary insight for practical optimisation of hard carbon-based SIB electrodes relies on combined analytical approaches.

In this review, various aspects of hard carbon electrodes for SIBs are discussed with an emphasis on the analytical tools that can be employed to investigate their structure and function. Overall, the review aims at providing the reader with comprehensive information about the state-of-the-art tools and techniques that can be employed to gain a detailed understanding of hard carbons and their application as the high-performance negative electrode material in alkali-ion batteries. Furthermore, in providing an overview of the recent innovations, this review is aimed to improve accessibility in utilising a greater variety of techniques to characterise hard carbon materials for SIBs and facilitate the use of combined analytical approaches. Characterisation using innovative and targeted analytical approaches is critical, particularly in moving towards the practicality of using battery chemistries beyond well-studied LIBs. It is the hope that fundamental insight gained from applying these techniques will help facilitate the design of the next-generation SIBs.

2. Materials characterisation

2.1. Background: physico-chemical properties

Hard carbon is synthesised from precursor materials rich in carbon and generally at high temperatures [31]. Synthetic polymeric feedstock materials such as polycrylonitrile fibers, phenolic resin, and resorcinol formaldehyde resin have been used to produce hard carbon [22]. Bearing in mind the increasing environmental concerns surrounding the manufacturing sector, there has been growing interest to improve sustainability [32] in the production of such carbonaceous materials especially using waste or biomass as precursors. Biomass materials such as algal blooms [33], starch [34], caltrop shell [35], waste tea [36], pistachio nut shell [37], rice husk [38], garlic peel [27], apple biowaste [39], and macadamia nut shell [2] among others have been successfully used for the synthesis of hard carbon.

The structural differences between graphite, soft carbons, and hard carbons are illustrated in figure 1(a). Although both soft and hard carbons are non-graphitic, soft carbon is graphitisable upon heat treatments at temperatures in the range of 1500 °C–3000 °C due to the weaker crosslinking between the graphene layers [40]. In contrast, the stronger crosslinking between the graphene layers in hard carbon inhibits the formation of the graphitic structure even at extremely high temperatures [41]. This difference arises in the synthetic process wherein hard carbons are prepared by the solid phase pyrolysis and soft carbons via gas or liquid phase pyrolysis [42].

Indeed, the scope for applicability of such a versatile range of precursor materials can be considered a benefit, however, their mixed compositions and a variety of synthesis routes can present challenges for characterisation, large-scale commercial implementation, and rational design of further materials. The diversity and lack of control over the composition of these starting materials imply that a cookie-cutter characterisation approach may not be applicable to collectively analyse hard carbons as a class of Na-ion
battery electrode materials. Moreover, the carbons produced from these precursors may also possess very different properties depending on the synthesis conditions [43].

Hard carbons generally possess a disordered structure that consists of randomly oriented and loosely stacked graphitic nanosheets (also called disordered turbostratic nanodomains) embedded in disordered amorphous regions, pores (which are usually empty spaces between the nanodomains), and various kinds of defects [46, 47]. The characteristic structure of hard carbons was proposed by Steven and Dahn [48] using a model named ‘House of Cards’ to establish the link between the hard carbon structure and the Na\(^+\) storage mechanisms. The model suggests that hard carbons have two distinct types of regions with varying microstructures resulting in two distinct Na\(^+\) storage mechanisms. One type of region comprises multiple parallel graphene layers (or graphitic nanodomains) which are embedded in the disordered domains. The other type of region constitutes empty space (porosity) between the graphitic nanodomains due to the random orientation of layers or domains against each other and the various kinds of defects. It has been proposed that sodium storage occurs in the hard carbons via a combination of two distinct mechanisms: (a) intercalation/insertion between the parallel graphene layers in the graphitic nanodomains and (b) the adsorption on the surface-active sites such as defects and nanopore filling which is also analogous to adsorption [49]. However, there is an ongoing debate about attributing the different phases of the storage to either adsorption or intercalation. In essence, both insertion into graphitic nanodomains (nanoscopic, 1–100 nm), as well as adsorption onto surface-active sites such as defects and nanopores (nanoscopic, 1–100 nm, microscopic, 100 nm–100 µm, macroscopic, >100 µm) play critical roles in the electrochemical performance of SIBs. The vast range, particularly in the scale of these features, adopted by various morphologies makes holistic characterisation and subsequent optimisation challenging to achieve.

The disordered structure of hard carbons complicates the use of conventional x-ray or neutron powder diffraction techniques (XRD and NPD, respectively) for characterisation of their atomic structure, as the dimensions of the coherently scattering graphitic domains are typically <20 Å resulting in limited Bragg scattering and very broad reflections (see figure 1(b)). However, if distinguishable from the background (e.g. with high quality data and/or partly graphitised), the main reflections can sometimes be used to determine the stacking axis \(d_{002}\) spacings of the graphitic parts of the carbon as well as to obtain a rough estimate of crystalline grain size using Scherrer analysis. In addition, XRD or NPD data may reveal the presence of crystalline impurities, e.g. from parasitic side reactions. Alternatively, advanced total scattering techniques (discussed later) may be used to extract more detailed information about local atomic structure from the diffuse scattering signal.
2.2. Microstructure

2.2.1. Microscopy

Hard carbon microstructure can influence Na adsorption processes into surface-reactive sites and pertinently the reversible capacity of SIBs related to these processes. Various forms of electron microscopy techniques such as scanning electron microscopy and high-resolution transmission electron microscopy (HRTEM) are generally accessible and can help directly visualise carbon microstructure, morphologies as well as interlayer/atomic distances (see figures 1(c) and (d)). Considering the intuitive insight that microscopy can provide, it can be tempting to use microscopy images to derive quantitative values such as graphitic interlayer spacing for the parts of the sample that are not wholly accurate/representative for the bulk of the material. It is important to consider that HRTEM images are generally limited to nanoscale dimensions and can therefore only represent nanoscale portions of the material at a time. Without large sampling sizes that adequately represent the overall sample, common morphological features such as defects, distortions in the crystal orientation, and other inhomogeneities can either be exaggerated or overlooked through microscopy images alone [19]. It can, therefore, be misleading to report the average spacing between the layers based solely on findings from microscopy in isolation. In characterising carbon morphology, it is therefore critical to supplement findings derived from microscopy with information from bulk techniques that statistically represent the sample properties.

For instance, the work by Beda et al combined multiple techniques including HRTEM, XRD, and Raman spectroscopy to characterise the structure/morphology of hard carbons derived from phenolic resins with spherical morphology [45, 50]. Beda et al mention that the use of spherical particles was motivated by their proposed high degree of compaction, shorter ion transport paths (thus improved mass transport), and smaller volume expansion arising from the formation of sodiated compounds. Whilst HRTEM was useful in providing a visual representation of the hard carbon architecture within their samples, graphitic crystallite size (Lc) and spacing between graphene layers were only loosely interpreted from the images to support values estimated from Scherrer analysis of XRD data. Additionally, I_D/I_G analysis from Raman spectroscopy measurements provided further evidence for the presence of both graphitised and disordered domains, justifying observed graphitic crystallite sizes through XRD analysis. In a work by Beda et al, a mean size of 3–4 µm of individual hard carbon spheres is found by using a combination of techniques. This provides insight into the overall homogeneity of the samples explored and rationalised the practicality of the fabrication processes towards industrial applications. Combining the strengths of multiple complementary techniques allowed for a well-rounded description of the carbon morphology that can be useful in directing the approach to designing further materials.

2.2.2. Specific surface area and pore morphology

Analysis of pore morphology can be used to infer adsorption capabilities of hard carbons. Gas adsorption–desorption equilibrium isotherms of N_2, Ar, or CO_2 adsorbates can be used to measure the specific surface area (SSA), pore size distribution, average pore size, and pore volume of porous materials using the Brunauer–Emmett–Teller (BET) theory and the Barrett–Joyner–Halenda method [51, 52]. The SSA and pore characteristics depend greatly on the type of adsorbate used and therefore, contradictory results may be obtained on the same sample depending on the adsorbate selected for the measurement [52]. N_2 has been the most commonly used adsorption gas for these measurements due to its easy availability in high purity, ease of accessibility of liquid nitrogen in most laboratories, and strong interaction with most solids [53]. However, it has some limitations, especially in the context of the micropore size distribution [54]. Ar is recommended by the International Union of Pure and Applied Chemistry (IUPAC) for surface area and pore size analysis due to better accessibility/diffusion into the micropores. Furthermore, CO_2 has even better access to small micropores up to 0.35 nm whereas both Ar and N_2 do not appear to diffuse into pores smaller than 0.45 nm [54]. In such cases, CO_2 can be used in tandem with Ar or N_2 to obtain a holistic picture of the pore characteristics of the material. According to IUPAC classification, micropores are <2 nm, mesopores range from 2–50 nm, and macropores are >50 nm in diameter [51]. Micropores can be further classified into ultra-micropores (<0.7 nm), medium-sized micropores (0.7–0.9 nm), and super-micropores (0.9–2 nm) [52]

The impact of surface area and pore size distribution on the performance of hard carbons is demonstrated in figure 2 based on the work by Zheng et al [55]. Three different types of hard carbon samples were derived from filter paper by different methods, namely (a) direct high temperature pyrolysis of the filter paper (DPC), (b) activation of DPC with KOH (DPC-A), and (c) chemical and thermal activation of filter paper (A-DPC). The BET SSA for DPC, DPC-A, and A-DPC carbons was found to be 431, 761, and 1472 m^2 g^-1, respectively. All the carbons exhibit type-I/IV isotherms as shown in figures 2(a) and (b).

A-DPC has a significant proportion of pore volume as micropores, which is likely to lead to the formation of...
Figure 2. (a) Isotherms corresponding to the N\textsubscript{2} adsorption-desorption. (b) Pore size distribution curves for carbons derived from filter paper, (c) voltage-capacity profiles for DPC, and (d) for A-DPC at a current density of 20 mA g\textsuperscript{−1}. Reproduced from [55]. CC BY 4.0.

A large and possibly excessive solid electrolyte interphase (SEI) layer. This difference in pore size distribution and surface area results in a poorer initial coulombic efficiency (ICE) for the A-DPC carbon as shown in figures 2(c) and (d) [55]. A poor ICE is problematic in full cell configuration as the charge carrier is used up, thereby, reducing energy density [56].

The pore morphology depends on numerous factors inter alia the precursor, pyrolysis temperature, and inert gas flow rate during synthesis. It is very intuitive and widely reported that the SSA of the carbon materials decreases with the increase in the pyrolysis temperature, which is often linked to the disappearance of the pores at higher temperatures [57]. The increase in the flow rate of the inert gas during the synthesis leads to decreased porosity as the CO\textsubscript{2} produced during the pyrolysis is quickly flushed away from the reaction environment avoiding its reaction with carbon in the sample and therefore preventing the formation of new pores by burn-off [40]. In addition, there are some pores that are clogged with the carbonaceous devolatisation products produced during the synthesis, and reaction with CO\textsubscript{2} can help open such pores. However, the high flow rate will likely hinder that process and therefore these pores may not be able to take part in the charge storage process.

The pores can also be either open-ended or closed and have broad size distributions [19]. The open pores are generally detrimental to the electrochemical performance of the hard carbon because of their role in the formation of an excessive SEI layer which often translates to poor ICE [58]. To that end, closed pores are considered more favourable as they can better accommodate the active ions by providing the storage sites. It remains challenging to accurately calculate the exact proportion of closed and open pores due to inherent
limitations of the measurement techniques. Nonetheless, the surface area and pore size distribution can be relatively well controlled to obtain a hierarchically porous carbon structure that is tunable by various chemical/thermal treatments before/after the pyrolysis [59]. Based on the discussion in this section, hard carbons with low SSA and unclogged large pores that are closed are likely to offer the best reversible performance. These characteristics appear to promote the reversible alkali metal ion exchange and minimise irreversible side reactions. Control over the SSA and porosity is essential to optimise the formation of SEI layer on the hard carbon electrodes during insertion/extraction reactions.

2.3. Graphitic nanodomains

2.3.1. Interlayer \(d_{002}\) spacing and crystallite size \(L_c\)

For graphitic nanodomains, a combination of techniques including XRD, Raman spectroscopy, and electron microscopy can be considered vital for reporting. The graphitic nanodomains are proposed to be related to LIB-like intercalation-based sodiation that may be occurring. Thus, characterisation of their properties (and how they compare to pristine graphite) may shed light on the conditions that promote/suppress these processes inside SIBs. Indeed, quantitative values that describe graphitic nanodomains are challenging to derive from routine techniques such as XRD-based Scherrer analysis, despite being commonly reported in this manner [60, 61]. Due to inherent limitations of these techniques, and inhomogeneities within samples and between batches, such quantitative values cannot always be precisely obtained across all types of materials. It is therefore important to avoid over-emphasising the significance of such quantitative values when reporting findings based on hard carbon morphologies. With adequate consideration of the limitations and degree of accuracy when interpreting data from such techniques, reporting quantitative results can be a valuable contribution to the general understanding of hard carbon morphologies.

Based on XRD analysis available in the literature, the lateral dimensions of the graphitic nanodomains in most hard carbons have been reported to be around 10–40 Å and number of layers stacked to be from two to six layers [40, 62]. Graphite is crystalline with the long-range order whereas hard carbons consist of disordered amorphous domains and relatively smaller graphitic nanodomains randomly distributed throughout the structure with short-range order and typically a larger interlayer distance \(d_{002}\) [3, 63]. Hard carbons also have pores between the randomly oriented graphitic nanodomains whose size depends on the size of these domains (typically, the smaller the graphitic nanodomains, the smaller the pores) resulting in a structure with more defects, different sodium diffusion pathways, and a larger number of sodium storages sites compared to traditional graphite where the sodium ions are considered to be ‘stored’ between the graphene layers [3]. In some investigations, hard carbons have been reported to have an average graphite-domain interlayer spacing of 3.7–4.2 Å [47, 64–66] which is higher than that for graphite (3.354 Å) [64, 67]. It is reported that unlike in the case of graphite, these parallel layers are not flat; rather they are curved, bent, or turbostratic [19]. With the increase in pyrolysis temperature, the (002) graphite-type peak shifts to higher 2\(\theta\) values leading to a decreased \(d_{002}\) spacing between the graphitic layers due to an increased relative ordering [40]. Furthermore, the Scherrer formula can be used to calculate the crystallite sizes \(L_c\) based on the (002) and (110) peaks, respectively [68]. Next, the \(d_{002}\) spacing and crystallite sizes \(L_c\) can be used to calculate the number \((N)\) of the graphene sheets stacked as per the equation \(N = L_c / d_{002}\) [49] where \(N\) is a good indicator of the structural ordering. A decrease in interlayer spacing and increase in the size of graphitic nanodomains results in the increased structural ordering, i.e. more bulk graphite like. According to Qiu et al, suitable \(d_{002}\) spacing (3.7–3.8 Å) and higher structural ordering generally enhances sodium insertion and therefore improve capacity achieved through these processes in the low potential plateau region in SIBs [49]. Monitoring variations in \(d_{002}\) spacing between samples and different electrochemical conditions can therefore be used to rationalise the enhancement or suppression of the intercalation/insertion processes and corresponding influence on the reversible capacity of the SIB.

2.3.2. I_D/I_G

Intrinsic structural defects and disorder in the structure are also relevant parameters that describe the overall hard carbon properties. As previously mentioned, based on work by Qiu et al, higher structural ordering with a suitable \(d_{002}\) spacing (3.7–3.8 Å) is generally desired as it is anticipated to enhance sodium intercalation/insertion between graphene layers and thus improve PRC capacity achieved through these processes in SIBs [49].

Hard carbons have distinct chemical environments due to the presence of a variety of defects such as vacancies and dangling bonds on the nanodomain edges [69]. The defects include vacancies, pores, curvature in the graphene sheets, the presence of the \(sp^3\) carbon linkages between the neighboring graphitic nanodomains. The level of disorder and defects in the \(sp^2\)-network of a carbon structure can be elucidated using Raman spectroscopy [70]. Unlike the typically defect-free graphene and graphite, which only have the
Figure 3. (a) Raman spectra of graphite and disordered carbon recorded at 514 nm with attribution of the main bands in the first, second, and third order regions. Reproduced from [75]. CC BY 4.0. Carbon motions in the (b) $E_{2g}$ G mode, and (c) $A_{1g}$ D breathing mode. Reprinted figure 1 with permission from [73], Copyright (2000) by the American Physical Society. (d) Raman spectra (acquired by using a 532 nm argon ion laser) of the hard carbon synthesised from macadamia nutshell biomass at 700 (M7), 900 (M9), and 1100 °C (M11). Reprinted with permission [2]. Copyright 2021, American Chemical Society.

G ($\sim 1585$ cm$^{-1}$) and 2D bands (satisfying the Raman selection rule) in the Raman spectrum, the defect-rich non-graphitic carbons such as those present in hard carbons have a Raman forbidden D band at $\sim 1345$ cm$^{-1}$, which is attributed to the disorder and defects in the structure (see figure 3(a)) [71]. The D band possessing $A_{1g}$ symmetry corresponds to the breathing mode in the six-atom rings and is activated only in the event of a defect [72]. Note, that the G band is caused by the relative motion of the $sp^{2}$ carbon atoms and has high-frequency $E_{2g}$ symmetry [73]. These modes are represented in figures 3(b) and (c).

The intensity ratio of the D and G bands ($I_D/I_G$) is widely used to study the evolution of the disorder and defect density in $sp^{2}$ carbon networks. This ratio was originally used to calculate the crystallite size of the $sp^{2}$ clusters ($L_a$), according to the formula $I_D/I_G = C(\lambda)/L_a$, also known as the Tuinstra-Koenig relation [74]. In this relation, $C(\lambda)$ is a constant of proportionality dependent on the excitation laser wavelength $\lambda$. It is worth noting that in some cases the integrated area (not the height or amplitude) of the D and G bands is used as the $I_D$ and $I_G$ values, respectively [71]. Although the D band is linked to the disorder and the defects in the structure, its interpretation is not as straightforward as it seems. The insights provided by the $I_D/I_G$ ratio vary significantly depending on the level of disorder in the carbon material. A three-stage classification of the disorder was proposed by Ferrari and Robertson which provides a basic framework to analyse the Raman
spectrum of carbons ranging from perfectly graphitic to amorphous carbons [73]. The first stage involves graphite to nanocrystalline graphite. The second stage covers nanocrystalline graphite to the amorphous carbon with maximum 20% \(sp^3\) sites. The third stage covers amorphous carbons with low levels of \(sp^3\) sites (\(\sim10–20\%\)) to high levels of \(sp^3\) sites (\(\sim85\%\)) with the gradual change of \(sp^3\) sites from rings to chains. It was shown that an increase in the \(I_D/I_G\) ratio in the first stage corresponds to the increasing defect-induced disorder in the structure as per the Tuinstra-Koenig relation. However, in stage two, the Tuinstra-Koenig relation is no longer valid once the crystallite size gets smaller than \(\sim20\) Å. The crystallite sizes of the graphitic nanodomains have been reported to range between 10 and 40 Å [40, 62] which should be considered while interpreting the Raman data. Nonetheless, for the carbons with disorder in stage 2, the development of the D band relative to the G band (increase in \(I_D/I_G\) ratio) has been found to correlate to the increased ordering in the structure [73]. Similar insights were reported elsewhere while interpreting the increased D-band area relative to the G-band with the increase in carbonisation temperature [76].

As an example, Raman data of hard carbons synthesised from macadamia nutshell biomass at 700, 900, and 1100 °C is shown in figure 3(d) [2]. The \(I_D/I_G\) ratio was calculated by fitting Voigt functions and was found to increase from 0.76 for the hard carbon synthesised at 700 °C to 0.98 for the one synthesised at 1100 °C. The crystallite size of the graphitic domains in these hard carbons based on the (002) graphite reflections in XRD data were calculated to be in the 10–13 Å range. As discussed earlier, for disordered carbons with a crystallite domain size smaller than 20 Å, a more dominant D mode can be attributed to the increased structural ordering and reduced defect density. This aligns very well with the results obtained in this work and further lends support to the disorder analysis of the carbons (that an increase in the D band intensity does not necessarily mean increased disorder).

Although not covered in this review, additional insights into structural characteristics can be derived from the detailed modelling of the peak shape, deconvolution, and the full width at half maximum. Overall, Raman spectroscopy is a very powerful technique that can provide valuable insights regarding the defect density and disorder in the structure if interpreted correctly. This in turn can help in optimising the structure to enhance the electrochemical performance of hard carbons.

3. Mechanistic characterisation

3.1. Background: mechanism

While hard carbon anodes are extensively used in SIBs, there is still no unanimous perspective on the Na\(^+\) insertion mechanisms that govern their electrochemical properties. As mentioned previously in section 2.1, in 2000, Stevens and Dahn proposed a ‘House of Cards’ model to explain the two main Na\(^+\) storage mechanisms that rely on graphitic nanodomains and microstructural porosity/defects [48]. However, there remains to be conflicting perspectives surrounding the interpretation, verification, and relative significance of Na\(^+\) storage via adsorption vs intercalation pathways.

Although this review mainly focuses on hard carbons for SIBs, it is also interesting to discuss the proposed storage of Li\(^+\) and K\(^+\) in the hard carbon structure and how/if it differs from the storage of Na\(^+\). Although all alkali-ions display some degree of both adsorption, intercalation, and pore filling, the contributions of each mechanism vary greatly among different ion systems. Na\(^+\) storage takes place primarily via adsorption and pore filling, while Li\(^+\) and K\(^+\) storage is proposed to occur predominantly via intercalation. The different alkali-ion insertion mechanisms are illustrated in figure 4.

These differences in insertion mechanism have largely been explained in the literature on the basis of their different ionic sizes and the thermodynamic stability of the intercalation compounds they form. However, other factors such as the choice of electrolyte solvents, sodium salts, and additives can have a significant impact on the extent and mechanism of insertion as well as on the formation of SEI layer [13, 14]. This has been discussed in detail in section 4.1. It should be emphasised that different alkali-ion based systems have distinct structural and morphological requirements for the host material, which necessitates the use of a range of complementary analytical techniques to understand and subsequently use as a basis to tune the characteristics of these carbon materials to suit the specific application. In the following section, we discuss various approaches which have been employed to obtain a deeper understanding of the charge storage mechanisms in hard carbons.

The Na\(^+\) insertion mechanisms involved in hard carbon charge storage in SIBs remain a subject of debate. According to Qiu et al, there are discrete characteristic features in electrochemistry that can arise from these mechanistic processes [49]. Adsorption onto defects/pores is associated with the initial sloping region that extends to voltages \(>0.1\) V (see figure 5(b)), whereas insertion into graphitic nanodomains is associated with the lower voltage plateau below 0.1 V (also known as plateau region capacity, PRC) that typically follows the initial sloping region. A significant portion of the electrochemical capacity delivered by
hard carbons is currently achieved as PRC at very low potentials that are ultimately reliant on the insertion between the graphene layers.

Although the main insertion pathway is generally accepted to occur via pore filling and/or adsorption within structural defects (due to relatively low stability of Na-graphite intercalated compounds or GICs) \[77–79\], considerable interest remains in activating/promoting Na\(^+\) intercalation by modification of SIB components such as the carbon electrode architecture and electrolyte composition \[17\]. Both of these mechanisms are illustrated in figures 5(a) and (b). This also raises the obvious question of whether multiple charge storage processes may be taking place concurrently or in a coupled manner with one type of process being more favoured in a particular spatial (on electrode) or potential (during function) region than the other. For instance, the adsorption on the defect sites could be more favourable in the sloping potential region, while the insertion/intercalation and pore filling might still be contributing to the charge storage but to a lesser extent until the onset of the PRC wherein the insertion/intercalation becomes the more favoured,
and adsorption becomes less prevalent. Nevertheless, it is critical to identify which region of the curve is governed by what process so that the changes observed in a particular region can be linked to the changes in the structure and morphology of the material. Figure 5(c) shows how the microstructure of the hard carbons changes with the increase in the pyrolysis temperature [80]. The crystallite size increases from 3.61 to 6.1 nm and the average number of parallel layers increases from 2 to 5 as the temperature increases from 900 °C to 1500 °C. At the same time, the interlayer spacing, porosity, and defects in the structure are expected to decrease significantly. These microstructural changes in the hard carbon constituents drive the changes in the capacities obtained in the sloping and PRC plateau region of the electrochemical curves.

3.2. Implications based on electrochemical results

3.2.1. Voltage profile analysis

Initial analysis of the voltage profiles of Na-ion cells can be used to infer the relative contributions of graphitic nanodomains and microstructure to the electrochemical performance of SIBs and corresponding charge storage mechanism.

A study aimed at elucidating the intercalation mechanism of sodium was undertaken on hard carbons prepared from lignin at temperatures ranging between 1000 °C and 1500 °C [43]. Figure 6(a) shows the voltage capacity profiles corresponding to the 1st, 2nd, 5th, and 10th cycle for the SIB with the hard carbon electrode prepared at 1300 °C and cycled at 50 mAh g⁻¹. The sloping and plateau regions can be clearly identified in the figure with the plateau region being in the <0.1 V range. Figure 6(b) shows how the capacity contributions from the sloping and plateau regions of the voltage-capacity profiles at 50 mA g⁻¹ evolve with the increase in the carbonisation temperature. The sloping region capacity decreases from 98 mAh g⁻¹ to 55 mAh g⁻¹ as the temperature used for hard carbon synthesis increases from 1000 to 1500 °C. On the other hand, the PRC increased first from 108 mAh g⁻¹ to 175 mAh g⁻¹ on increasing the temperature from 1000 to 1300 °C after which it started decreasing, ultimately reaching ~120 mAh g⁻¹ at 1500 °C. It is widely accepted that, as the carbonisation temperature increases, the structure tends to transition from short-range structural order to a structure with a higher degree of graphitisation and lower defect density and porosity facilitated by considerable collapse of the micropores [43, 81, 82]. The various types of defects are responsible for the adsorption capacity and the insertion between the graphene sheets is responsible for the intercalation/insertion capacity. Considering that the sloping region capacity decreases with the decreasing number of defect sites suggests that the sloping region can possibly be linked predominantly to the adsorption capacity. Similarly, the increase in the PRC with increased structural ordering essentially means that there are larger number of and/or bigger sizes of graphitic nanodomains present in the structure to effectively facilitate a larger extent of insertion/intercalation between the graphene layers; indicating that the plateau region can be attributed to the insertion/intercalation capacity.

A strong argument that supports the adsorption mechanism for the sloping region of the voltage profile is the broad energy distribution for adsorption sites. Defects in hard carbons are not very well defined and can be of many different types such as pores, vacancies, curvature in the graphene sheets, and the sp³ carbon linkages between the neighbouring graphitic nanodomains. Such a wide distribution of morphological
defects is likely to result in a sloping sodiation profile in the capacity-voltage plot due to a range of sodiation voltages unique to each defect type [69]. This observation indicates that the sloping region is representative of the adsorption capacity whereas a narrow-range energy distribution in the plateau region is indicative of the intercalation between the graphene layers. This is further illustrated in figure 7 where glassy carbon has the smallest sloping capacity due to the lowest defect concentration and the S-1100 sample has the largest sloping capacity due to the highest defect concentration [69]. These observations support the adsorption-insertion mechanism of charge storage for hard carbons in SIBs.

3.2.2. Galvanostatic intermittent titration technique (GITT)

GITT measurements can be used to infer the charge storage mechanism in SIBs by evaluating the kinetic properties in different regions of the voltage profile. Using GITT, the Na-ion diffusion coefficient can be calculated using Fick’s second law and can be plotted as a function of the potential [83].

Figure 8 [69] shows a GITT profile where the diffusion is found to be faster in the sloping region suggesting a fast initial Na\(^+\) insertion on the sites that are easily accessible. Considering that the surface sites, such as defects, are more accessible than the interlayer spacings between the graphene layers and the nanopores, the sloping region on the potentiogram is likely to arise from the adsorption of Na\(^+\) on the defect sites.

Furthermore, a very sharp drop in diffusivity is observed near the onset of the plateau/PRC region at 0.1 V. The drop continues until 0.05 V where diffusion is at its minimum and \(dQ/dV\) is at its maximum.
(figure 8(b)). After this minimum, the diffusivity starts to increase again until 0.01 V (cut-off voltage). A possible explanation is the presence of two distinct Na$^+$ insertion mechanisms in the low-voltage plateau/PRC region. The region from 0.1 to 0.05 V with very low diffusivity could be due to the intercalation of ions between the graphene layers. The more facile diffusion in the 0.05–0.01 V region could be explained by the facilitation of easy access to the space between the layers by the Na-ions inserted in the 0.1–0.05 V region. However, this is unlikely due to the aforementioned instability of the Na-graphitic intercalation compounds. Alternatively, this phenomenon could be attributed to the adsorption of Na$^+$ on the pore surfaces with $sp^3$ configuration which can also be classified as the pore filling. In essence, by offering insight on ion diffusivity, GITT analysis can complement galvanostatic/potentiostatic testing results in ascertaining the pathways for Na$^+$ insertion related to certain redox features.

A majority of the reported works on the use of GITT for the characterisation of the storage mechanism in hard carbons for SIBs point to the adsorption-intercalation-pore filling mechanism (the sloping region of the voltage-capacity profile is attributed to the adsorption capacity, initial plateau region to the intercalation capacity, and the region following that is attributed to the pore-filling capacity) which attests to its reliability and places it as a very useful tool in the elucidation of the charge storage mechanism [22, 69, 76, 83, 85]. Nonetheless, formulating a precise picture of the charge storage phenomenon in hard carbons has proved to be very challenging. The major reason for the complexity is the inhomogeneous structure of the hard carbons, which can often lead to contradictory findings from averaging techniques such as XRD, Raman, and NMR when compared with the findings from localised techniques such as HRTEM [86]. Another major reason is likely to be the presence of various potential mechanisms which are often overlapping. A single analytical tool cannot be sensitive to all of these mechanisms. Therefore, the interpretation of the charge storage mechanism has sometimes resulted in very different conclusions depending on the techniques used. Based on the discussion so far, it is clear that there is significant ongoing debate among the research community between the adsorption-intercalation, adsorption-intercalation-pore filling, and intercalation-adsorption mechanisms in hard carbons when employed in SIBs and further investigation is thus needed to unambiguously elucidate the mechanism.

### 3.3. Characterising sodiation and local structure evolution of hard carbons

#### 3.3.1. $^{23}$Na solid-state nuclear magnetic resonance spectroscopy

Solid-state nuclear magnetic resonance (ssNMR) spectroscopy can also provide useful insights into the charge storage mechanism in hard carbons. The local chemical environment and the atomic structure of a material play a major role in dictating the charge storage mechanism and the resultant overall capacity. Stratford et al used $^{23}$Na ssNMR to propose a charge storage mechanism by examining the electronic structure of the sodium inserted in the hard carbon [84]. In this work, they studied four different hard carbon samples, namely, Carbon A, Carbon B, Carbon 1100 °C, and Carbon 1500 °C. Carbon A and Carbon B are commercially available carbons produced by Kureha Battery Materials Japan Co., Ltd and Faradion Ltd, respectively. Glucose was used as the precursor material to synthesise Carbon 1100 °C and Carbon 1500 °C. They cycled the cells at C/20 rate (1 C = 300 mA g$^{-1}$) in 0.005–2.0 V range for the operando ssNMR measurements and corresponding ssNMR data is shown in figure 9. All the patterns have strong peaks corresponding to sodium metal and NaPF$_6$ in the electrolyte at 1135 ppm and ∼10 ppm, respectively.

Voltage profiles for all the samples exhibited two distinct regions: sloping region and a plateau/PRC region. During the sloping region, changes in the diamagnetic region are noticed at only around 0 ppm, however, these changes are hard to visualise due to a relatively strong signal from the electrolyte in the same region. Nonetheless, the analysis of ssNMR data suggested that ionic sodium insertion takes place during the sloping region. Next, during the plateau region, a new peak appears which gradually shifts to higher frequencies as the discharge process progresses. The chemical shift at the end of the discharge varies from 760 to 960 ppm across the hard carbons tested. The changes in the contribution of sloping and plateau regions towards total capacity was linked to the aforementioned $^{23}$Na chemical shift at the end of the discharge. The larger chemical shift was attributed to the enhanced contribution from the Knight shift and increase of the Na 2 s density of states at the Fermi level which was associated with the formation of metallic sodium during the plateau region. These processes were ascribed to Na$^+$ insertion in between the graphene layers and also to the filling of pores with sodium clusters [84, 87]. The carbons with higher ratio of plateau/slope capacity (relatively larger contribution from plateau region) were found to display larger $^{23}$Na chemical shift at the end of the discharge. For instance, the Carbon 1500 °C (ratio of plateau/slope capacity = 2.55) showed a shift of 940 ppm compared to 850 ppm shown by Carbon 1100 °C (ratio of plateau/slope capacity = 1.62). The differences in the final shift in the carbons was attributed to the differences in the structure of the carbons in terms of degree of order and pore size distribution. It was suggested that a range of tools and techniques need to be used in the investigation of materials as complex as hard carbons. NMR can serve as a useful tool in this regard.
3.3.2. In situ/operando XRD and pair distribution function analysis

Analysis through diffraction techniques can shed light on Na\textsuperscript{+} insertion mechanisms and their influence on both the hard carbon microstructure and graphitic nanodomains.

In XRD, assessment of the evolution of the graphitic (002) stacking axis reflection can provide insight on the occurrence or non-occurrence and magnitude of Na\textsuperscript{+} insertion mechanisms into graphitic nanodomains, and thus the contribution of these processes to the overall SIB capacity. Figures 10(a) and (b) show in situ XRD data collected on partially graphitised hard carbon during discharge vs Li\textsuperscript{+}/Li and Na\textsuperscript{+}/Na, respectively. As highlighted by the dashed lines in the figure, Li\textsuperscript{+} insertion leads to a shift in the (002) stacking axis reflection, which indicates that some degree of intercalation takes place between the graphitic layers. Notably, the (002) peak gradually shifts back towards the initial position during the de-insertion of Li\textsuperscript{+}, indicating a reversible process. However, no peak shift is observed when discharging the cell to 0 V vs Na\textsuperscript{+}/Na suggesting that Na\textsuperscript{+} insertion is likely occurring by a different mechanism [20].

Notably, in recent years, total scattering with pair distribution function (PDF) analysis has become increasingly essential as a means for examining the local atomic structure of materials [88]. This insight can be especially valuable in understanding the local structure and its evolution upon electrochemical treatment in hard carbon materials. As the low crystallinity of hard carbons results in limited Bragg scattering, this approach, which takes advantage of the diffuse scattering signal, may yield pertinent information. In a recent study by Mathiesen et al., the authors used operando synchrotron x-ray total scattering with PDF analysis to examine the local structural response of hard carbon anodes during Na\textsuperscript{+} and Li\textsuperscript{+} insertion [89]. The characterisation was carried out using a custom-made capillary-based electrochemical cell setup illustrated in figure 11(a). The PDF analysis (see figures 11(b)–(d)) revealed a clear correlation between in-plane and interplane interatomic distances and the state of charge. In-plane and interplane elongation and contraction were observed upon cycling and was attributed to a reversible charge transfer between sodium and the antibonding orbitals of the upper π band of the graphene sheet, suggesting the possibility of some intercalating behavior. Notably, an irreversible decrease in order was observed upon discharge which was consistent with an observed capacity loss. An analogous lithium insertion experiment showed a similar but less pronounced structural variation upon equivalent cycling. In essence, unprecedented insight on the local structure interactions between Na\textsuperscript{+} and graphitic nanodomains can be obtained from PDF analysis. This insight is particularly useful to assess the reversibility of Na\textsuperscript{+} insertion processes into graphitic nanodomains, and thus their contribution to the overall SIB performance.
Figure 10. In situ x-ray diffraction patterns and corresponding discharge curve vs (a) Li and (b) Na collected from hard carbon nanofibers treated at 2200 °C (∼2.5 nm). The peak marked with * arises due an electrolyte side reaction. [20] John Wiley & Sons. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

3.3.3. Raman spectroscopy to study the evolution of structural defects and disorder
Pertinently, the evolution of structural defects and disorder can be monitored to reveal further insight on the reversibility of insertion mechanisms into graphitic nanodomains. Changes in the microstructure during the charging and discharging process could be identified using a combination of analytical techniques. Although XRD has been widely used to investigate structural changes, it is generally not very conclusive due to the poor crystallinity of hard carbon. For instance, in a study using the pinecone biomass-derived hard carbon anodes in SIBs, the crystallite size was calculated with the Scherrer equation based on the (002) and (100) peaks in the XRD patterns [90]. However, this may not represent an accurate picture of the carbon structure as both (002) and (100) peaks are very broad. Raman spectroscopy has emerged as a very powerful technique in this regard.

A large proportion of research articles use ex situ analysis on the extracted electrodes to understand the structural changes during cycling. For instance, hard carbons synthesised from sucrose at 1000 and 2000 °C, were reported to not undergo intercalation based on ex situ Raman and XRD analysis even though the charge/discharge curves have a very wide plateau region [91]. This analysis was based on the observation that the G-band position remains unchanged in all the ex situ Raman spectra collected at different states of charge in both ester-based and ether-based electrolytes. It was stated in this work that for the sodium intercalation to take place, there should be a shift in the G-band. Furthermore, even the XRD patterns acquired at different states of charge, no shift was noticed in (002) peak which was further attributed to the lack of intercalation. Likewise, in lignin-derived hard carbon intercalation was dismissed based on the absence of shape change and peak position shift for the G-band in the ex situ Raman analysis [92]. Are these observations a result of.
the equilibration and extraction procedure necessary for ex situ analysis or do they truly represent the mechanism of the material? This question can be answered by using the operando Raman spectroscopy. In Raman data, the intercalation/insertion of Na\(^+\) ions between the graphene layers in the highly crystalline graphitic materials has been reported to result in G-band shape change (splitting of the G-band with the new peak becoming stronger as the sodiation advances) \[91\]. In the case of hard carbons, the intercalation/insertion of Na\(^+\) ions between the graphene layers in the graphitic nanodomains has been shown to cause the broadening of the G-band followed by its disappearance, often also accompanied by the shifting of the G-band as the sodiation progresses \[92, 93\]. An operando Raman spectroscopy study on a commercial hard carbon (Carbotron PS(F) with single point BET surface area is 7.0 m\(^2\) g\(^{-1}\); Kureha Corp) was performed to elucidate the Na\(^+\) insertion mechanism \[93\]. Figures 12(a)–(e) represents the Raman spectra acquired after different stages of Na\(^+\) insertion. Before Na\(^+\) insertion, the carbon featured well-defined D (\(\sim\)1350 cm\(^{-1}\)) and G (\(\sim\)1600 cm\(^{-1}\)) bands but as Na\(^+\) insertion increases, the D and G bands become less defined. The SEI layer forms at around 0.8 V vs Na/Na\(^+\) due to the reaction of the Na\(^+\) passing through the interface and is in part due to the decomposition of the carbonates present in the electrolyte on the pristine electrode surface \[94\]. During cycle 1, the energy and width of the D and G bands remain constant during the initial SEI formation phase \[93\]. During the initial period of SEI formation up to \(\sim\)50 mAh g\(^{-1}\), the background is almost flat. However, there is a considerable increase in the slope of the background after the aforementioned period which is linked to the increased fluorescence due to the formation of the SEI. The changes in the spectra in terms of the background slope can possibly be tracked and quantified to better understand the SEI formation. After the SEI formation, the G-band gradually shifts to lower energies from \(\sim\)1600 cm\(^{-1}\) at the start of sloping region of the voltage profile to \(\sim\)1560 cm\(^{-1}\) at the end of sloping region \[93\]. The shifting of the G-band to lower energies in the sloping region was associated with intercalation in the graphene-like layers in the turbostratic nanodomains in the hard carbons. The G-band energy did not change in the low voltage plateau/PRC region. The authors suggested that this was indicative of the absence of intercalation in the plateau region. Furthermore, the authors suggested that the capacity in the plateau region was attributed to the formation of sodium clusters in the pores. This work supports the intercalation followed by pore filling mechanism of charge storage in hard carbons which is in contrast to inference from some of the studies discussed in section 3.2. This demonstrates the conflicting...
perspectives surrounding SIB mechanistic processes, and that there is no universally accepted charge storage mechanism for hard carbons.

Nevertheless, Raman spectroscopy is a very powerful technique for probing the charge storage mechanism in hard carbons. Therefore, another example is discussed using *in situ* Raman spectroscopy for SIBs. In this study by Huang *et al.*, the authors used N-doped hard carbons as anodes in SIBs [95]. Doping the hard carbons with heteroatoms such as N, P, B, S, etc has been shown to introduce a larger number of active sites in the carbon architecture and enhanced Li$^+/Na^+$ storage capability. This has been linked with better charge transfer resulting into improved electrical conductivity and rate performance compared to undoped hard carbons [96, 97]. *In situ* Raman spectroscopy was used to elucidate the charge storage mechanisms in terms of adsorption and intercalation in N-doped hard carbon nanoshells (N-GCNs) as shown in figure 13 [95]. The *in situ* Raman spectra are shown in figure 13(a) and corresponding charge/discharge profiles during the 1st cycle at 0.25 A g$^{-1}$ are shown in figure 13(b). The shape, intensity, and position of the D ($\sim$1350 cm$^{-1}$) and G ($\sim$1600 cm$^{-1}$) bands are expected to change with the adsorption and intercalation/insertion into the structure. The gradual decrease in the intensity of D-band is reported to be
linked to the adsorption of Na\(^+\) on the defect sites. The adsorbed ions reportedly limit the breathing motion of the sp\(^3\) atoms in the rings at the edge planes. The G-band was found to shift to lower wavenumbers as the discharge process continued in the low voltage region. This was attributed to charge transfer occurring during the adsorption of Na\(^+\) and the formation of SEI layer. However, a similar shift in G-band position to lower wavenumber was related to intercalation in graphitic nanodomains in the earlier example by Weaving et al [93]. There are some clear disagreements in the literature on the interpretation of changes observed in Raman spectra during electrochemical cycling and further investigation is necessary to reach a unanimous interpretation. Nonetheless, this work by Huang et al states that there is no evident decrease in the intensity of G-band and that there is no obvious intercalation into the graphitic nanodomains due to the larger ionic radius of Na\(^+\), suggesting the charge storage is mainly adsorption driven. Although the interpretation of Raman data and charge storage mechanism for hard carbon in SIB systems is still under debate, it is worth reiterating the fact that the charge storage mechanism greatly depends on the hard carbon microstructure which in turn depends on precursor material, synthesis conditions, etc. Therefore, the observations reported by Huang et al regarding the absence of intercalation in hard carbon electrode for SIBs could hold true, if at all, only in the context of their work shown in figure 13 and might not be a general comment on all hard carbons. This is shown to emphasise that in situ Raman can serve as a useful tool to identify the charge storage mechanism in hard carbons if the findings are inferred correctly and possibly not all hard carbons behave the same owing to their unique microstructures.

4. Monitoring effects to surface speciation

4.1. SEI layer and its impact on ICE

The largest challenge hindering practical applications of hard carbons as anode materials for SIBs is often considered to be its poor ICE [98]. The ICE of an electrode material is defined as the ratio of the 1st charge capacity to the 1st discharge capacity in a half-cell setup. The main reasons behind the low ICE are the
formation of SEI layer during the initial cycling, irreversible trapping of Na\(^+\) in the defects, pores, etc, and side reactions [56]. Hard carbons generally have a high SSA that facilitates excess consumption of electrolyte. This promotes the formation of SEI layers but also the formation of irreversible decomposition products or excessive SEI layers. In a work by Bommier et al, hard carbons were synthesised at 800 °C–1100 °C yielding SSAs between 24 and 266 m\(^2\) g\(^{-1}\) [58]. The carbon synthesised at 1100 °C (BET SSA of 24 m\(^2\) g\(^{-1}\)) delivered an initial reversible capacity of 335 mAh g\(^{-1}\) whereas the one synthesised at 800 °C (BET SSA of 266 m\(^2\) g\(^{-1}\)) delivered an initial reversible capacity of 200 mAh g\(^{-1}\). This example illustrates that very high SSA can often prove to be detrimental to the performance of these materials. It is, therefore, critical to tune the structure of these carbons to facilitate the formation of a thin and stable SEI layer.

Furthermore, the thickness and the composition of the SEI layer have a defining role in the cycling behavior of the electrodes. As discussed earlier, limiting the porosity and SSA of the hard carbons is a plausible and viable solution to control the SEI layer. In addition, surface coatings and electrolyte optimisation by selecting suitable solvents, sodium salts, and additives can help in the formation of a thin and stable SEI layer along with an improved ICE [99–102]. The electrolytes are prepared by mixing a suitable sodium salt in a single or mix of organic ether or ester-based solvents with occasional use of additives. NaPF\(_6\) and NaClO\(_4\) are the most widely used salts for SIBs with sporadic use of the salts such as sodium bis(fluorosulfonyl)imide (NaFSI) [103], sodium bis(trifluoromethylsulfonyl)imide (NaTFSI), and NaCF\(_3\)SO\(_3\) [104]. Ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC), propylene carbonate (PC), dimethyl ether (DME), tetraethylene glycol dimethyl ether (TEGDME), and diethylene glycol dimethyl ether (DEGDME) are some of the most commonly used solvents reported in the literature [56]. Fluoroethylene carbonate is the most widely used additive in the electrolytes for SIBs aimed at forming a stable SEI layer. Further, different solvents interact differently with hard carbons and typically feature different redox potentials. Therefore, it is intuitive that different electrolytes are likely to form SEI layers with varying compositions. In a work aimed at optimising the electrolyte, it was found that NaPF\(_6\) in EC/PC was the best performing electrolyte with high ionic conductivity and low viscosity [105]. The hard carbon reportedly formed a stable SEI layer with this electrolyte resulting in an improved cycling stability, enhanced ICE, and rate performance. In a study performed by Patra et al, 3 mol dm\(^{-3}\) NaFSI in PC/EC electrolyte with conductivity of 6.3 mS cm\(^{-1}\) and viscosity of 23 cP helped in forming a stable organic-inorganic balanced SEI layer which was mainly composed of (CH\(_2\))\(_n\) and NaF [106]. The SEI layer reportedly exhibited good passivation ability, excellent stability, and facilitated fast Na\(^+\) transport. Owing to the formation of a stable and thin SEI layer, the ICE was found to increase from 59% for 1 mol dm\(^{-3}\) NaPF\(_6\) in EC/PC, to 60% for 1 mol dm\(^{-3}\) NaFSI in PC/EC to 85% for 3 mol dm\(^{-3}\) NaFSI in PC/EC.

Furthermore, ether-based co-intercalating electrolytes have attracted considerable attention due to their ability to take part in Na\(^+\) storage process in the form of solvated ions [56, 107]. The use of ether-based electrolytes enables the formation of a thinner and more stable SEI layer resulting in a relatively better ICE and rate performance than ester-based electrolytes. In a work aimed at understanding the differences in the SEI layers formed with ether (1 M NaCF\(_3\)SO\(_3\) in diglyme) and ester-based (1 M NaCF\(_3\)SO\(_3\) in 1/1 volume ratio of EC/DEC) electrolytes, Li et al made use of x-ray photoelectron spectroscopy (XPS) based depth profiling technique to obtain the elemental composition of SEI layer at different etching depths in the range of 0–25 nm [108]. In both cases, the signals were detected for C, O, F, and Na for all the different etching depths scanned. The SEI surface with the ether-based electrolytes was found to be comprised of organic compounds and the internal SEI was found to be composed of more inorganic compounds. The inorganic compounds have been reported to form a thin and stable SEI layer with a smaller charge transfer resistance and lower energy barrier, due to their typical tendency to remain localised [109]. In contrast, the case of ester-based traditional electrolytes, a larger proportion of organic compounds was found throughout the SEI layer [108]. This was attributed to the easier reduction of carbonate solvents on the Na metal surface due to their higher reduction potentials as compared with the ether solvents, which results in the formation of a larger proportion of undesirable organic species in the SEI [109, 110]. Furthermore, organic compounds have been reported to be more porous than inorganics leading to the formation of a thicker SEI layer with a higher energy barrier owing to higher resistance to charge transfer [109]. This was presented as the reason for better rate performance when using ether-based electrolytes.

In one particular example, Zhu et al compared the performance of loofah sponge-derived hard carbon in ether and ester-based electrolytes [104]. They used NaOTf in DEGDME (1 mol L\(^{-1}\) NaCF\(_3\)SO\(_3\) in diethylene glycol dimethyl ether) as the ether-based electrolyte and NaCO in EC/DEC (1 mol L\(^{-1}\) NaClO\(_4\) in ethylene carbonate/dimethyl carbonate) as the ester-based electrolyte. The ether-based electrolytes resulted in a much higher PRC at high rates. For instance, for the carbon synthesised at 1300 °C (LSI300), the PRC increased from 16 mAh g\(^{-1}\) in the ester-based electrolytes to 143 mAh g\(^{-1}\) in the ether-based electrolytes. The rate performance of LSI300 was further probed by cycling it at very high current rates. An exceptional rate performance was exhibited by the material wherein a discharge capacity of 210, 142, 75, 60, 45, and
Figure 14. (a) Nyquist plots to compare EIS results for highSAC (1410 m² g⁻¹) and lowSAC (24 m² g⁻¹) carbons as electrodes. The samples were discharged to various levels during the 1st discharge before performing ex situ measurements. CV curves of (b) lowSAC, (c) highSAC at 0.2 mV s⁻¹. Reprinted from [58] Copyright (2014), with permission from Elsevier.

34 mAh g⁻¹ at the rate of 5, 10, 20, 30, 50, and 80 C, respectively was obtained. Such performance at high rates was attributed to the formation of a thin and stable SEI layer that restrained ongoing electrolyte decomposition. The insights obtained in this work demonstrate the importance of choosing the right electrolyte.

Next, FEC is an effective additive that has been widely used for SIBs [56]. Its use has been found to form a passivation film that suppresses the electrolyte decomposition resulting in a smoother, thinner, and stable SEI layer as revealed by hard and soft XPS [111]. FEC has a higher reduction potential than most other electrolyte solvents such as EC, DEC, PC, diglyme, etc, and sodium salts [112, 113]. This results in its preferential reduction before other electrolyte constituents to form an insoluble and stable passivating inorganic surface layer that is ionically conducting and electronically insulating to protect the electrode surface [111].

The discussion in this section illustrates that the selection of type and concentration of various electrolyte constituents has a great effect on the SEI layer, resultant ICE, and long-term performance of a battery.

It has been established that excessive growth of the SEI is detrimental to the battery performance [114]. Consequently, the SEI layer should be investigated in detail to identify its constituents which can help in understanding the SEI formation mechanism and therefore in optimising it. That said, the SEI is often one of the most experimentally challenging components to characterise.

4.2. SEI characterisation

In work by Bommier et al, electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were used to monitor SEI formation when using sucrose derived hard carbon electrodes in SIBs (figure 14) [58]. Hard carbons were synthesised at 800 °C–1100 °C and an activation time with CO₂ between 0 and 10 h yielding SSAs between 24 and 1400 m² g⁻¹. Based on BET analysis, the carbon synthesised at 1100 °C without CO₂ activation had the lowest surface area of 24 m² g⁻¹ (lowSAC) while the one synthesised at
1000 °C and activated at 900 °C for 10 h had the highest surface area of 1410 m² g⁻¹ (highSAC).

Figure 14(a) shows the EIS measurements performed on the lowSAC and highSAC carbons at the initial, 0.5, 0.1 and 0.01 V during the 1st discharge. The diameter of the semicircle on the Nyquist plot is related to resistivity for the charge transfer at the interface. The diameters of the semicircles on the Nyquist plots increase at a larger extent for highSAC than lowSAC upon discharge, implying higher resistivity for the charge transfer at the interface with higher surface area. The larger resistivity at the initial stages of discharge can be linked to the formation of thicker and more extensive SEI layer in high SAC. This can further be explained based on the CV measurements as shown in figures 14(b) and (c). As the majority of the SEI formation is expected to occur during the 1st cycle [58], the differences in the area enclosed by CV curves during 1st and 2nd cycles can be linked to the extent of SEI formation [58]. The areal difference for lowSAC and highSAC was found to be 6% and 26%, respectively indicating the substantial difference in extent of SEI formation. In addition, the CV curve for the lowSAC carbon exhibits an anodic peak which is attributed to the oxidation of the Na metal during the extraction of deposited Na metal from the carbon structure. The absence of this peak in highSAC can be linked to the electrochemical irreversibility of the deposited Na metal which in part explains the large irreversible capacity loss in materials possessing high surface area.

In another study, the CV curves from the first three cycles performed between 0 and 3 V on reed straw biomass derived hard carbon synthesised at 900 °C–1500 °C [80] are shown in figure 15. There is an irreversible peak at ~0.5 V which disappears after the 1st cycle. This peak is ascribed to the formation of the SEI layer due to its irreversible nature. This peak becomes weaker as the synthesis temperature increases due to the decreased defect density, porosity, and SSA. In essence, both EIS and CV measurements provide valuable insights into understanding the SEI formation however care must be taken, as such measurements are indicative and often require further experimental support.

5. Conclusion

In this review, the structure and charge storage mechanism of hard carbons have been discussed from the standpoint of available characterisation techniques and the findings obtained from their use that can be
useful in the hard carbon research. This includes discussions of the examination of the unique atomic- and micro-structure of hard carbons using powder diffraction, Raman spectroscopy, and BET surface area analysis; followed by the investigation of the charge storage mechanism by voltage profile analysis, in situ/operando XRD, in situ Raman spectroscopy, 23Na ssNMR spectroscopy, and GITT. The issue of poor ICE in hard carbons is discussed next wherein XPS, EIS, and CV are shown as key laboratory techniques to examine and gain an enhanced understanding of the formation of the SEI layer. Each individual characterisation technique may have several limitations and may not be able to provide an unequivocal understanding of the system. Thus, a combined approach involving multiple complementary techniques is often necessary. Furthermore, hard carbons might behave differently in other alkali-ion battery systems or during electrochemical cycling and may thus require in situ and operando techniques in order to probe the true mechanisms at play. The range of analytical tools/techniques presented here may help researchers gain a comprehensive understanding of the impact morphology, surface area, porosity, defect structure, graphitic domains, and other parameters on the electrochemical performance parameters, thereby ‘finding’ the optimal material with appropriate physico-chemical properties for commercial SIB applications.

Data availability statement

No new data were created or analysed in this study.

Acknowledgments

The authors would like to thank the support from our funding programs, Australian Research Council, Research Training Program, Future Fellowships and Discovery program (FT200100707 and DP200100959), the ACME Foundation, the Carlsberg Foundation (Grant Nos. CF18-0519 and CF19-0143), the Spanish Ministry of Universities (Ministerio de Universidades) and the European Union—NextGenerationEU through a Maria Zambrano—atraction of international talent fellowship grant.

ORCID iDs

Uttam Mittal  https://orcid.org/0000-0001-5905-2997
Lisa Djuandhi  https://orcid.org/0000-0002-4523-9221
Neeraj Sharma  https://orcid.org/0000-0003-1197-6343
Henrik L Andersen  https://orcid.org/0000-0003-1847-8427

References

[1] Togonon J J H, Chiang P-C, Lin H-J, Tsai W-C and Yen H-J 2021 Pure carbon-based electrodes for metal-ion batteries Carbon Trends 3 100035
[2] Kumar U, Wu J, Sharma N and Sahajwalla V 2021 Biomass derived high areal and specific capacity hard carbon anodes for sodium-batteries Energy Fuels 35 1820–30
[3] Xie F, Xu Z, Guo Z and Titirici M-M 2020 Hard carbons for sodium-ion batteries and beyond Prog. Energy 2 042002
[4] Cresce A V et al 2017 Solvation behavior of carbonate-based electrolytes in sodium ion batteries Phys. Chem. Chem. Phys. 19 574–86
[5] Liu T, Zhang Y, Chen C, Lin Z, Zhang S and Lu J 2019 Sustainability-inspired cell design for a fully recyclable sodium ion battery Nat. Commun. 10 1963
[6] Willuhn M 2021 CATL claims to have made sodium-ion batteries a commercial reality (available at: www.pv-magazine.com/2021/07/29/catl-claims-to-have-made-sodium-ion-batteries-a-commercial-reality/)
[7] Maisch M 2021 Sodium-ion battery tech gets commercial testing in UK (available at: www.pv-magazine.com/2022/01/21/sodium-ion-battery-tech-get-commercial-testing-in-uk/)
[8] Asenbauer J, Eisenmann T, Kuenzel M, Kazzazi A, Chen Z and Bresser D 2020 The success story of graphite as a lithium-ion anode material—fundamentals, remaining challenges, and recent developments including silicon (oxide) composites Sustain. Energy Fuels 4 5387–416
[9] Andersen H L, Djuandhi L, Mittal U and Sharma N 2021 Strategies for the analysis of graphite electrode function Adv. Energy Mater. 11 2102693
[10] Xiao B, Rojo T and Li X 2019 Hard carbon as sodium-ion battery anodes: progress and challenges ChemSusChem 12 133–44
[11] Moriwake H, Kuvabara A, Fisher C A J and Ikubara Y 2017 Why is sodium-intercalated graphite unstable? RSC Adv. 7 36550–4
[12] Kim H, Hong J, Yoon G, Kim H, Park K-Y, Park M-S, Yoon W-S and Kang K 2015 Sodium intercalation chemistry in graphite Energy Environ. Sci. 8 2963–9
[13] Park J, Xu Z-L and Kang K 2020 Solvated ion intercalation in graphite: sodium and beyond Front. Chem. 8 432
[14] Jache B and Adelhelm P 2014 Use of graphite as a highly reversible electrode with superior cycle life for sodium-ion batteries by making use of Co-intercalation phenomena Angew. Chem., Int. Ed. 53 10169–73
[15] Kim H, Hong J, Park Y-U, Kim J, Hwang I and Kang K 2015 Sodium storage behavior in natural graphite using ether-based electrolyte systems Adv. Funct. Mater. 25 534–41
Kim H, Kim H, Ding Z, Lee M H, Lim K, Yoon G and Kang K 2016 Recent progress in electrode materials for sodium-ion batteries. *Adv. Energy Mater.* 6 1600943

Tsai P, Chung S-C, Lin S and Yamada A 2015 *Ab initio* study of sodium intercalation into disordered carbon. *J. Mater. Chem. A* 3 9763–8

Xu Z-L, Yoon G, Park K-Y, Park H, Tamwattana O, Joo Kim S, Seong W M and Kang K 2019 Tailoring sodium intercalation in graphite for high energy and power sodium ion batteries. *Nat. Commun.* 10 2598

Zhao L, Hu Z, Lai W, Tao Y, Peng J, Miao Z, Wang Y, Chou S, Liu H and Dou S 2021 Hard carbon anodes: fundamental understanding and commercial perspectives for Na-ion batteries beyond Li-ion and K-ion counterparts. *Adv. Energy Mater.* 11 2002704

Zhang B, Ghimbeu C M, Laberty C, Vix-Guterl C and Tarascon J-M 2016 Correlation between microstructure and Na storage behavior in hard carbon. *Adv. Energy Mater.* 6 1501588

Wang M, Yang Y, Yang Z, Gu L, Chen Q and Yu Y 2017 Sodium-ion batteries: improving the rate capability of 3D interconnected carbon nanofibers thin film by boron, nitrogen dual-doping. *Adv. Sci.* 4 1604068

Wang K, Jin Y, Sun S, Huang Y, Peng J, Luo J, Zhang Q, Qiu Y, Fang C and Han J 2017 Low-cost and high-performance hard carbon anode materials for sodium-ion batteries. *ACS Omega* 2 1687–95

Zhang X, Zhu G, Wang M, Li J, Lu T and Pan L 2017 Covalent-organic-frameworks derived N-doped porous carbon materials as anode for superior long-life cycling lithium and sodium ion batteries. *Carbon* 116 686–94

Li W, Zeng L, Yang Z, Gu L, Wang J, Liu X, Cheng J and Yu Y 2014 Free-standing and binder-free sodium-ion electrodes with ultralong cycle life and high rate performance based on porous carbon nanofibres. *Nanoscale* 6 693–8

Yang J, Zhou X, Wu D, Zhao X and Zhou Z 2017 S-doped N-rich carbon nanosheets with expanded interlayer distance as anode materials for sodium-ion batteries. *Adv. Mater.* 29 1604108

Elizabeth I, Singh B P, Trikha S and Gopukumar K 2016 Bio-derived hierarchically macro-meso-micro porous carbon anode for lithium/sodium ion batteries. *J. Power Sources* 329 412–21

Selvamani V, Ravikumar R, Suryanarayanan V, Velasutham D and Gopukumar S 2016 Garlic peel derived hierarchical N-doped porous carbon anode for sodium/lithium ion cell. *Electrochim. Acta* 190 337–45

Li X, Paranatham M P, Akato K, Naskar A K, Levine A M, Lee B J, Kim S-O, Zhang J, Dai S and Manthiram A 2016 Tire-derived carbon composite anodes for sodium-ion batteries. *J. Power Sources* 316 232–8

Kumar U, Goonetilleke D, Gaikwad V, Pramudita J C, Joshi R K, Sharma N and Sahajwalla V 2019 Activated carbon from E-waste plastics as a promising anode for sodium-ion batteries. *ACS Sustain. Chem. Eng.* 7 10310–22

Zhu X, Jiang X, Liu X, Xiao L and Cao Y 2017 Aqua green water Igor cell to synthesis low-cost and high-performance hard carbon as promising sodium-ion battery anodes from sorghum stalk waste. *Green Energy Environ.* 2 310–5

Hwang J-Y, Myung S-T and Sun Y-K 2017 Sodium-ion batteries: present and future. *Chem. Soc. Rev.* 46 3529–614

Dou X, Hasa I, Saured D, Vaalma C, Wu L, Buchholz B, Bresser D, Komaba S and Passerini S 2019 Hard carbons for sodium-ion batteries: structure, analysis, sustainability, and electrochemistry. *Mater. Today* 23 87–104

Meng X, Savage P E and Deng D 2015 Trash to treasure: from harmful algal blooms to high-performance electrodes for sodium-ion batteries. *Environ. Sci. Technol.* 49 12543–50

Kim Y, Kim J-K, Vaalma C, Bae G H, Kim G-T, Passerini S and Kim Y 2018 Optimized hard carbon derived from starch for rechargeable seawater batteries. *Carbon* 129 564–71

Wang P, Fan L, Yan L and Shi Z 2019 Low-cost water cellophane derived hard carbon with high initial Coulombic efficiency for sodium-ion battery anodes. *J. Alloys Compd.* 775 1028–35

Pei L, Cao H, Yang L, Liu P, Zhao M, Xu B and Gao J 2020 Hard carbon derived from waste tea biomass as high performance anode material for sodium-ion batteries. *Ionics* 26 5335–42

Kim K, Lim D G, Han C W, Ousswald S, Ortalan V, Youngblood J P and Pol V G 2017 Tailored carbon anodes derived from biomass for sodium-ion storage. *ACS Sustain. Chem. Eng.* 5 8720–8

Rybarczyk M K, Li Y, Qiao M, Hu Y S, Titirici M M and Lieder M 2019 Hard carbon derived from rice husk as low cost negative electrodes in Na-ion batteries. *J. Energy Chem.* 29 17–22

Wu L, Buchholz D, Vaalma C, Griffin G A and Passerini S 2016 Apple-biowaste-derived hard carbon as a powerful anode material for Na-ion batteries. *ChemElectroChem* 3 292–8

Irizarri E, Prououch A and Palacin M R 2015 Review—hard carbon negative electrode materials for sodium-ion batteries. *J. Electrochem. Soc.* 162 A2476–82

Soltani N, Bahrami A, Bielkiewicz D, Gom secretary T, and Mikkilä N 2021 Progress and challenges in using sustainable carbon anodes in rechargeable metal-ion batteries. *Prog. Energy Combust. Sci.* 87 100929

Perveen T, Siddiq M, Shahzad N, Ihsan R, Ahmad N and Shahzad M I 2020 Prospects in anode materials for sodium-ion batteries—a review. *Renew. Sustain. Energy Rev.* 119 109549

Alvin S, Cahyadi H S, Hwang J, Chang W, Kwak S K and Kim J 2020 Revealing the intercalation mechanisms of lithium, sodium, and potassium in hard carbon. *Adv. Energy Mater.* 10 2000283

Nishi Y 2001 The development of lithium secondary batteries. *Chem. Rec.* 1 406–13

Beda A, Rabuel F, Morcrette M, Knopf S, Taberna P-L, Simon P and Matei Ghimbeu C 2021 Hard carbon key properties allow for the achievement of high Coulombic efficiency and high volumetric capacity in Na-ion batteries. *J. Mater. Chem. A* 9 1743–58

Li Z, Jian Z, Wang X, Rodriguez-Pérez J A, Bomnier C and Ji X 2017 Hard carbon anodes of sodium-ion batteries: undervalued rate capability. *Chem. Commun.* 53 2610–3

Wang Q, Zhu X, Liu Y, Fang Y, Zhou Z and Bao J 2018 Rice husk-derived hard carbons as high-performance anode materials for sodium-ion batteries. *Carbon* 127 658–66

Stevens D A and Dahm J R 2000 High capacity anode materials for rechargeable sodium-ion batteries. *J. Electrochem. Soc.* 147 1271–9

Qu S et al 2017 Manipulating adsorption—insertion mechanisms in nanostructured carbon materials for high-efficiency sodium-ion storage. *Adv. Energy Mater.* 7 1700403

Beda A, Taberna P-L, Simon P and Matei Ghimbeu C 2018 Hard carbons derived from green phenolic resins for Na-ion batteries. *Carbon* 139 248–57

Barrett E P, Joyner L G and Halenda P P 1951 The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms. *J. Am. Chem. Soc.* 73 373–80

Bardestani R, Patience G S and Kaliaguine S 2019 Experimental methods in chemical engineering: specific surface area and pore size distribution measurements—BET, BJH, and DFT. *Can. J. Chem. Eng.* 97 2781–91
[53] Raja P M V and Barron A R BET Surface Area Analysis of Nanoparticles (available at: https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Physical_Methods_in_Chemistry_and_Nano_Science_(Barron)/02%3A_Physical_and_Thermal_Analysis/2.03%3A_BET_Surface_Area_Analysis_of_Nanoparticles)

[54] Anonymous A Choosing the right gas for surface area and pore size analysis (available at: https://wiki.anton-paar.com/au-en/gas-adsorption-for-surface-area-and-pore-size-analysis/)

[55] Zheng P, Liu T and Guo S 2016 Micro-nano structure hard carbon as a high performance anode material for sodium-ion batteries Sci. Rep. 6 35620

[56] Zhang M, Li Y, Wu F, Bai Y and Wu C 2021 Boost sodium-ion batteries to commercialization: strategies to enhance initial Coulombic efficiency of hard carbon anode Nano Energy 82 105738

[57] Kumar U, Maroufi S, Rajarao R, Mayyas M, Mansuri I, Joshi R K and Sahajwalla V 2017 Cleaner production of iron by using waste macadamia biomass as a carbon resource J. Clean. Prod. 158 218–24

[58] Bommier C, Luo W, Gao W-Y, Greaney A, Ma S and Ji X 2014 Predicting capacity of hard carbon anodes in sodium-ion batteries using porosity measurements Carbon 76 165–74

[59] Kumar U, Gaikwad V, Mayyas M, Sahajwalla V and Joshi R K 2018 Extraordinary supercapacitance in activated carbon produced via a sustainable approach J. Power Sources 394 140–7

[60] Holder C F and Schaar R E 2019 Tutorial on powder x-ray diffraction for characterizing nanoscale materials ACS Nano 13 7359–65

[61] Weidenthaler C 2011 Pitfalls in the characterization of nanoporous and nanosized materials Nanoscale 3 792

[62] Buie E R, George A E and Dahn J R 1999 Model of micropore closure in hard carbon prepared from sucrose derived hard carbon J. Mater. Chem. A 9 27140–69

[63] Zheng Y, Wang Y, Lu Y, Hu Y-S and Li J 2017 A high-performance sodium-ion battery enhanced by macadamia shell derived hard carbon anode Nano Energy 39 489–98

[64] Komaba S, Murata W, Ishikawa T, Tabuuchi N, Ozeki T, Nakayama T, Ogata A, Gotoh K and Fujiwara K 2011 Electrochemical Na insertion and solid electrolyte interphase for hard-carbon electrodes and application to Na-ion batteries Adv. Funct. Mater. 21 3850–67

[65] Gaddam R R, Jiang E, Amirvand N, Annamalai P K, Martin D J, Kumar N A and Zhao X S 2017 Spinifex nanocellulose derived hard carbon anodes for high-performance sodium-ion batteries Sustain. Energy Fuels 1 1090–7

[66] Wen Y, He K, Zuo Y, Han F, Xu Y, Matsuda I, Ishii Y, Cumings J and Wang C 2014 Expanded graphite as superior anode for sodium-ion batteries Nat. Commun. 5 4033

[67] González-Díez, Montes-Morán M A, Suárez-Ruiz I and Garcia A B 2004 Structural characterization of graphite materials prepared from anthuraceous of different characteristics: a comparative analysis 18 365

[68] Bommier C, Surta T W, Dolgos M and Ji X 2015 New mechanistic insights on Na-ion storage in non-graphitizable carbon Nano Lett. 15 3888–92

[69] Lucchesi M M, Stavale F, Ferreira E H M, Vilani C, Moutinho M V O, Capaz R B, Achete C A and Jorio A 2010 Quantifying ion-induced defects and Raman relaxation length in graphene Carbon 48 1592–7

[70] Eckmann A, Felten A, Mishchenko A, Britnell L, Krupek R, Novoselov K S and Casiraghi C 2012 Probing the nature of defects in graphene by Raman spectroscopy Nano Lett. 12 3925–30

[71] Ferrari A C and Basko D M 2013 Raman spectroscopy as a versatile tool for studying the properties of graphene Nat. Nanotechnol. 8 235–46

[72] Ferrari A C and Robertson J 2000 Interpretation of Raman spectra of disordered and amorphous carbon Phys. Rev. B 61 14095–107

[73] Tuinstra F and Koenig J L 1970 Raman spectrum of graphite J. Chem. Phys. 53 1126–30

[74] Merlen A, Buijnsters J and Pardanaud C 2017 A guide to and review of the use of multiwavelength Raman spectroscopy for characterizing defective aromatic carbon solids: from graphene to amorphous carbons Coatings 7 153

[75] Xia J, Yan D, Guo L, Dong X, Li W and Lu A 2020 Hard carbon nanosheets with uniform ultramicropores and accessible functional groups showing high realistic capacity and superior rate performance for sodium-ion storage Adv. Mater. 32 2000447

[76] Wang H-G, Yuan S, Ma D-L, Zhang X-B and Yan J-M 2015 Electrosynthetic materials for lithium and sodium rechargeable batteries: from structure evolution to electrochemical performance Energy Environ. Sci. 8 1660–81

[77] Yang J et al 2021 From micropores to ultra-micropores inside hard carbon: toward enhanced capacity in room-temperature sodium-ion storage Nano-Micro Lett. 13 98

[78] Euchner H, Vinayan B P, Reddy M A, Fichtner M and Groß A 2020 Alkali metal insertion into hard carbon—the full picture J. Mater. Chem. A 8 35620

[79] Li X, Zeng X, Ren T, Fan L, Zhang F and Shi Z 2018 Facile hydrothermal treatment route of reed straw-derived hard carbon for high-performance sodium-ion batteries Sustain. Energy Fuels 1 1090–7

[80] U Mittal et al
[90] Zhang T, Mao J, Liu X, Xuan M, Bi K, Zhang X L, Hu J, Fan J, Chen S and Shao G 2017 Pinecone biomass-derived hard carbon anodes for high-performance sodium-ion batteries RSC Adv. 8 41504–11

[91] Bai P, He Y, Zou X, Zhao X, Xiong P and Xu Y 2018 Elucidation of the sodium-storage mechanism in hard carbons Adv. Energy Mater. 8 1703217

[92] Lin X, Liu Y, Tan H and Zhang B 2020 Advanced lignin-derived hard carbon for Na-ion batteries and a comparison with Li and K ion storage Carbon 157 316–23

[93] Weaving J S, Lim A, Millichamp J, Neville T P, Ledwoch D, Kendrick E, McMillan P F, Shearing P R, Howard C A and Brett D J L 2020 Elucidating the sodiation mechanism in hard carbon by operando Raman spectroscopy ACS Appl. Energy Mater. 3 7474–84

[94] Yabuuchi N, Kubota K, Dahbi M and Komaba S 2014 Research development on sodium-ion batteries Chem. Rev. 114 11636–82

[95] Huang S, Li Z, Wang B, Zhang J, Peng Z, Qi R, Wang J and Zhao Y 2018 N-doping and defective nanographitic domain coupled hard carbon nanoshells for high performance lithium/sodium storage Adv. Funct. Mater. 28 1706294

[96] Dong J et al 2017 Improved Li+ storage through homogeneous n-doping within highly branched tubular graphitic foam Adv. Mater. 29 1603692

[97] Xie D, Xia X, Zhong Y, Wang Y, Wang D, Wang X and Tu J 2017 Exploring advanced sandwiched arrays by vertical graphene and N-doped carbon for enhanced sodium storage Adv. Energy Mater. 7 1601804

[98] Wan Y, Liu Y, Chao D, Li W and Zhao D 2022 Recent advances in hard carbon anodes with high initial Coulombic efficiency for sodium-ion batteries accepted (https://doi.org/10.1016/j.nanoms.2022.02.001)

[99] Che H, Yang X, Yu Y, Pan C, Wang H, Deng Y, Li L and Ma Z-F 2021 Engineering optimization approach of nonaqueous electrolyte for sodium ion battery with long cycle life and safety Green Energy Environ. 6 212–9

[100] Shen L, Shi S, Roy S, Yin X, Liu W and Zhao Y 2021 Recent advances and optimization strategies on the electrolytes for hard carbon and P-based sodium-ion batteries Adv. Funct. Mater. 31 2006066

[101] Nagmani K A and Puravankara S 2022 Optimizing ultramicroporous hard carbon spheres in carbonate ester-based electrolytes for enhanced sodium storage in half-/full-cell sodium-ion batteries Batter. Energy 1 20220007

[102] Palomares V, Serras P, Villaluenga J, Hueso K B, Carretero-González J and Rojo T 2012 Na-ion batteries, recent advances and present challenges to become low cost energy storage systems Energy Environ. Sci. 5 5884

[103] Wróbel P, Kubisik P and Eilmes A 2021 NaFSI and NaTFSI solutions in ether solvents from monoglyme to poly(ethylene oxide)—a molecular dynamics study J. Phys. Chem. B 125 10293–303

[104] Zhu Y-E, Yang L, Zhou X, Li F, Wei J and Zhou Z 2017 Boosting the rate capability of hard carbon with an ether-based electrolyte for sodium ion batteries J. Mater. Chem. A 5 9528–32

[105] Ponrouch A, Marchante E, Courty M, Tarascon J-M and Palacin M R 2012 In search of an optimized electrolyte for Na-ion batteries Energy Environ. Sci. 5 8572

[106] Patra J, Huang H-T, Xue W, Wang C, Helal A S, Li J and Chang J-K 2019 Moderately concentrated electrolyte improves solid–electrolyte interphase and sodium storage performance of hard carbon Energy Storage Mater. 16 146–54

[107] Bommier C and Li X 2018 Electrolytes, SEI formation, and binders: a review of nonelectrode factors for sodium-ion battery anodes Small 14 1703576

[108] Li K et al 2019 Evolution of the electrochemical interface in sodium ion batteries with ether electrolytes Nat. Commun. 10 725

[109] Seh Z W, Sun J, Sun Y and Cui Y 2015 A highly reversible room-temperature sodium metal anode ACS Cent. Sci. 1 449–55

[110] Park M S, Ma S B, Lee D J, Im D, Doo S-G and Yamamoto O 2015 A highly reversible lithium metal anode Sci. Rep. 4 3815

[111] Dahbi M, Nakano T, Yabuuchi N, Fujimura S, Chihara K, Kubota K, Son J-Y, Cui Y-T, Oji H and Komaba S 2016 Effect of hexafluorophosphate and fluoroethylene carbonate on electrochemical performance and the surface layer of hard carbon for sodium-ion batteries ChemElectroChem 3 1856–67

[112] Liu X, Zhou J, Xu Z and Wang Y 2020 Atomic thermodynamics and microkinetics of the reduction mechanism of electrolyte additives to facilitate the formation of solid electrolyte interphases in lithium-ion batteries RSC Adv. 10 163502–12

[113] Hou T, Yang G, Raiput N N, Self J, Park S-W, Nanda J and Persson K A 2019 The influence of FEC on the solvation structure and reduction reaction of LiPF6/EC electrolytes and its implication for solid electrolyte interphase formation Nano Energy 64 103881

[114] Song J, Xiao B, Lin Y, Xu K and Li X 2018 Interphases in sodium-ion batteries Adv. Energy Mater. 8 1703082