Chapter 2

Carbon Anodes for Sodium-Ion Batteries

Syed Mustansar Abbas1*, Muhammad Iftikhar1,2, Ata-ur-Rehman2

1 Nanoscience and Technology Department, National Centre for Physics, Islamabad, Pakistan
2 Department of Chemistry, Quaid-e-Azam University, Islamabad, Pakistan
*qau_abbas@yahoo.com

Abstract

Current attempts have shown great prospect of substituting lithium-ion batteries (LIBs) with their rival named as Sodium-ion batteries (SIBs), as both share similar chemistry while lithium being scarce and expensive in comparison to the earth crust rich sodium. The poor performance of SIBs anode has restricted its development in the past. Recently, a significant amount of research has been focused on anode materials for SIBs. Carbonaceous anodes have become viable SIB anodes providing high safety, abundant resources, and nontoxicity. In this chapter, the prominent sodium storage capabilities of some potent carbonaceous anodes namely hard carbon, graphite, carbon nanofibers, graphene, biomass derivatized carbon and heteroatom-doped carbon, have been discussed.

Keywords

Sodium-Ion Battery, Anode, Carbon Nanofiber, Hard Carbon, Graphene

Contents

1. Introduction ........................................................................................................32
2. Overview of SIBs electrode materials .................................................................33
3. Carbon anode materials for advanced SIBs ..........................................................36
   3.1 Graphite as anode for SIBs .........................................................................36
   3.2 Hard carbon as anode for SIBs .................................................................38
   3.3 Graphene as anode for SIBs .....................................................................40
   3.4 Carbon nanofibers as anode for SIBs .........................................................45
   3.5 Biomass-derived carbon as anode for SIBs .................................................48
3.6 Heteroatom-doped carbon materials as anode for SIBs

References

1. Introduction

The rapid development of modern society in various fields has exponentially increased energy consumption. Because of the depletion in fossil fuel, there is larger interest in sustainable green renewable energy and non-exhaustive sources like solar, waves and wind etc. However, for consistent use of this sustainable energy in an electrical grid, a suitable energy storage device is essential. In this context, a surge has risen for advanced energy storage and conversion technologies that can fulfil globally increasing energy needs and prevent environmental pollution. Rechargeable batteries or secondary batteries are one of the most suitable among all available technologies because of their tuneability, high energy storage and conversion capabilities, and ease of fabrication and maintenance [1, 2]. Today, lithium-ion batteries (LIBs), as well as sodium-ion batteries (SIBs), are the most widely studied rechargeable battery systems.

LIBs are the most popular and globally recognized power sources of the present time pertaining to the several advantages that they offer like high energy density, lasting cycle life, eco-friendly and lightweight [3, 4]. In last decade or so, there is a vibrant swing towards SIBs research due to some drawbacks associated with LIBs like high cost, limited lithium resources, safety problems and complex cycling protocols [2, 5-9]. Being a part of alkali metals in the periodic table both lithium, and sodium share similar electrochemistry. Owing to the low cost of sodium, (only ∼3% compared with Li source) SIBs are expected to be more suitable for large-scale grid storage applications [10], geographically even distribution (23600 ppm compared with 20 ppm of Li) [11] and can be drained to zero charge, making it easy for shipment and storage while LIBs must retain some charge for transportation and storage [12]. SIBs offer another economical potential in the form of using aluminium current collector for anode as it does not form an alloy with aluminium and thus eliminating the risk of corrosion while LIBs utilize more costly copper anode [13, 14]. However, some inherent shortcomings associated with SIBs like the apparently larger ionic radius of Na⁺ (1.02 Å as compared to 0.76 Å for Li⁺), heavier mass of Na (23 g mol⁻¹ as equated to 6.9 g mol⁻¹ for Li) make SIBs to demonstrate low energy and power density in comparison to LIBs [12, 15]. Therefore, it is highly demanded that suitable anode, cathode, separators and electrolytes may be searched to increase the efficiency of most cost-effective storage devices in the form of SIBs. A brief comparison is tabulated between sodium and lithium (Table 1).
Table 1  Evaluation of physical characteristics for LIBs and SIBs. Reproduced with permission [13]. Copyright 2019 The American Chemical Society

<table>
<thead>
<tr>
<th>Property</th>
<th>LIBs</th>
<th>SIBs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative atomic mass</td>
<td>6.94</td>
<td>23.00</td>
</tr>
<tr>
<td>Mass-to-electron ratio</td>
<td>6.94</td>
<td>23.00</td>
</tr>
<tr>
<td>Shannon’s ionic radii/Å</td>
<td>0.76</td>
<td>1.02</td>
</tr>
<tr>
<td>E° (vs SHE)/V</td>
<td>-3.04</td>
<td>-2.71</td>
</tr>
<tr>
<td>Melting point/°C</td>
<td>180.5</td>
<td>97.7</td>
</tr>
<tr>
<td>Theoretical capacity of metal electrodes/mAh g⁻¹</td>
<td>3861</td>
<td>1166</td>
</tr>
<tr>
<td>Theoretical capacity of metal electrodes/mAh cm⁻³</td>
<td>2062</td>
<td>1131</td>
</tr>
<tr>
<td>Theoretical capacity of ACoO₂/mAh g⁻¹</td>
<td>274</td>
<td>235</td>
</tr>
<tr>
<td>Theoretical capacity of ACoO₂/mAh cm⁻³</td>
<td>1378</td>
<td>1193</td>
</tr>
<tr>
<td>Molar conductivity in ACIO₄/PC/S cm² mol⁻¹</td>
<td>6.54</td>
<td>7.16</td>
</tr>
<tr>
<td>Desolvation energy in PC/kJ mol⁻¹</td>
<td>218.0</td>
<td>157.3</td>
</tr>
<tr>
<td>Coordination preference</td>
<td>octahedral and tetrahedral</td>
<td>octahedral and prismatic</td>
</tr>
</tbody>
</table>

2. Overview of SIBs electrode materials

Fig. 1 shows a simplified schematic diagram of a working SIB consisting of an anode and cathode mounted on their respective current collectors, electrolyte, and separator film [16]. The working principle is almost the same as that for LIBs following reversible intercalation/deintercalation between anode and cathode. During charging, the desodiation takes place from the cathode as it is oxidized and Na⁺ ions are inserted into anode as reduction takes place. During the discharging cycle, the anode gets oxidized releasing the Na⁺ ions that travel through electrolyte towards the cathode, which is reduced during sodiation process and electrons flow through the external circuit [17].

Over the past few decades, SIBs have been recorded with many distinct anode and cathode materials. Some of the most widely reported cathodes include phosphates, sulfides, polyanions, sulphates, layered oxides, fluorides, Prussian blue and various types of organic polymers. Layered oxides provide high potency as cathode material for SIBs, however, their multiphase and irreversible transitions during cycling result in lower rate performance and capacity decay [18]. Several types of layered oxides have been reported that are generally classified into O3 or P2 type depending on the accommodation of Na⁺ ions at octahedral or prismatic sites, respectively. Some of the representative layered oxides include O3-NaNi₁/₃Mn₁/₃Co₁/₃O₂ (~120 mAh g⁻¹ discharge capacity at C/10 up to 50th cycle) [19] P2-Na₀.₆₇Ni₀.₂₅Mg₀.₁Mn₀.₆₅O₂, [20] (140 mAh g⁻¹ discharge capacity and
energy density of 335 Wh kg$^{-1}$ and P2-Na$_{2/3}$[Fe$_{1/2}$Mn$_{1/2}$]O$_2$ [21] (~149 mAh g$^{-1}$ discharge capacity at 12 mA g$^{-1}$ at the end of 30 cycles). Due to their rigid, perovskite-like framework structure and ambient temperature synthetic protocols, the Prussian blue and its structural analogues have proved suitable insertion hosts for SIBs [22-25]. Some of the representative materials in this class include KFe$_2$(CN)$_6$ [22], KMnFe(CN)$_6$ (80–120 mAh g$^{-1}$) [13, 22], Na$_4$Fe(CN)$_6$ (~90 mAh g$^{-1}$) [26]. The defects in the framework structure, together with low electronic conductivity, hamper their use as standard cathode for SIBs [27, 28]. Polyanion compounds are considered as research hotspot for SIBs cathode because of their high operating voltage, diversity in structure and excellent cycling performance, however, they also suffer from capacity fading upon prolonged cycling [29]. Some of the representative cathodes of this class include, NASICAON-type Na$_3$V$_2$(PO$_4$)$_3$-C [30] (~90 mAh g$^{-1}$ at 2340 mA g$^{-1}$ after 10000 cycles), NaFe(SO$_4$)$_2$ [31] (~80 mAh g$^{-1}$ at 0.1 C for 80 cycles), NaFePO$_4$ [32] (144.3 mAh g$^{-1}$ after 300 cycles at 0.1 C). Recently organic compounds have received special emphasis owing to their resource abundance, eco-friendly, recycling potential, good designability and low cost [33]. Various combination compounds of organic tetrasodium salts (Na$_4$C$_8$H$_2$O$_6$, Na$_2$C$_8$H$_2$O$_6$/Na$_4$C$_8$H$_2$O$_6$, and Na$_4$C$_8$H$_2$O$_6$/Na$_6$C$_8$H$_2$O$_6$) [34] can deliver specific capacities around 180 mAh g$^{-1}$ with excellent Coulombic efficiencies (C.E), however, organic compounds have poor inherent conductivity and they are prone to be dissolved in organic electrolytes, which limits their practical applicability. Fig. 2a shows a comparative summary of the representative cathode materials used for SIBs [35].

**Figure 1.** Scheme showing the operating principle of SIBs and most usual anode, cathode, electrolyte, binders and additive used. Reproduced with permission [16]. Copyright 2019 Royal Society of Chemistry.
In comparison to cathodes, less attention has been given to anode materials for SIBs. Presently most of the SIB anode research is focused on carbonaceous materials, metal oxides, carbon-based composites and alloy based materials. Conjugated aromatic polymers are also a strong contender for SIB anode but their complicated synthesis protocols limit their use in the commercial cell. A layered 2D conjugated polymer with substantial porosity was prepared by polymerization of tetrabromopolyaromatic monomers and has been used as an anode for SIBs with successful capacity outcomes (∼79 mAh g⁻¹ (70%) at 5 A g⁻¹ after 7700 cycles) [36]. Various metal oxides [37-40] and metal sulfides [41-43] have been widely searched in this direction and they present high capacities with good cycle life, however, the usual volume variation problem is much more pronounced for metal oxides and metal sulfides for SIBs anode. Titanium-based oxides, [15, 44, 45] especially anatase TiO₂ is reported as a potential anode for SIBs whereby it presents high capacities at higher current rates with good stability (134 mAh g⁻¹ (95%) at 3.35 A g⁻¹ after 4500 cycles). Similarly, Sn [38, 44, 46] is well known for its high potential as anode materials and reported Sn₁₀Bi₁₀Sb₈₀ alloy [47] shows 620 mAh g⁻¹ of discharge capacity at the end of the 100th cycle. Some iron-based sulfide material also display value as anode like Fe₃S₄ [48] is reported to undergo conversion reaction yielding FeS₂, and FeS quantum size particles that help to gain the extra electrochemical stability and hence the discharge capacities achieved are quite encouraging (275 mAh g⁻¹ at 20 A g⁻¹ after 3500 cycles). Fig. 2b shows a comparative summary of the representative anode materials used for SIBs [35]. Among these anodes,
the highest attention is paid to different carbon-based materials, therefore, this chapter focusses on different kinds of carbon-based materials that have been explored as SIB anodes.

3. Carbon anode materials for advanced SIBs

3.1 Graphite as anode for SIBs

Graphite is one of the major carbon allotropes found naturally and can be prepared from petroleum or coal at high temperatures. Graphite has the layered framework in an ABAB-hexagonal stacking with graphene layers which are packed in combination with the weak Van der Waals forces. The interlayers are separated at a distance of which is suitable for hosting guest metal ions especially Li\(^+\) by forming graphite-intercalation compounds (GICs). It is regarded as a semi-metal because of its effective electronic composition that offers both thermal and electrical conductivity [49].

Commercially graphite has been the most commonly applied LIB anode caused by the formation of LiC\(_6\) (372 mAh g\(^{-1}\)) during intercalation however; its structure seems less favourable for forming Na-C binary compounds when used as anode for SIBs [50] and in this case, it may give only 31 mAh g\(^{-1}\) theoretical capacity for NaC\(_{70}\) [51]. Several computational studies have been conducted to explore the reason for this low capacity and density functional theory (DFT) studies have revealed the formation of NaC\(_6\) and NaC\(_8\) intercalated structures that suffer high instability due to the incompatibility of the larger and heavier Na\(^+\) ions to accommodate in to the graphitic layers, stretching in C-C bonds lengths and high Na/Na\(^+\) redox potential [52, 53].

Scientists have attempted to tune up the interlayer lattice distance of graphite to accommodate more Na\(^+\) ions and have reported graphitic network with an interlayer spacing of 4.3 Å (typical graphite d-spacing = 3.354 Å) and they have reported capacities as good as 284 mAh g\(^{-1}\) (20 mA g\(^{-1}\)) for 2000 cycles [54]. The Fig. 3 illustrates an interlayer expansion of graphite electrode during sodium storage process [54]. Some other studies have suggested that choosing an appropriate solvent with graphite can help enhance Na\(^+\) ion intercalation by co-intercalation effect following equation 1 [55].

\[
C_n + e^- + A^+ + y \text{ sol} u \leftrightarrow A^+(\text{sol} u)_y C_n^-
\]  
(Eq. 1)
For example, using diglyme as a solvent for electrolyte the capacity observed was 100 mAh g\(^{-1}\) under the current rate of 37 mA g\(^{-1}\) for 1000 cycles [55] and by using ether-based electrolyte the capacity increased to 150 mAh g\(^{-1}\) under 100 mA g\(^{-1}\) current and retain to 127 mAh g\(^{-1}\) at the completion of 300 cycles [56]. Several other solvent combinations (DME, EC/DEC, TEGDME and DEGDME) with sodium electrolytes (NaClO\(_4\), NaPF\(_6\), NaCF\(_3\)SO\(_3\)) were also evaluated and their phase transitions were measured by operando X-ray diffraction technique [57].

The electrochemical performance of SIBs seems to be considerably affected by the electrolyte components with graphite and it has been found that the co-intercalation effect of electrolyte helps reduce the usual repulsive interactions of Na\(^+\) ions and graphite together with the higher solvation energy and increased stability of the Na-solvent complex [50, 57]. Along with the favourable effects of co-intercalation the drawbacks include; the higher consumption of electrolyte, high intercalation voltage leading to the low energy density of full sodium ion cell and large volume expansions (~350 %) [58].

Till now the insertion/intercalation of Na\(^+\) ions within graphite layers has proved impractical, so alternative schemes for bulk power storage systems are needed to augment the thermodynamic stability of sodium-graphite intercalation compounds.
3.2 Hard carbon as anode for SIBs

Hard carbon is the material most frequently recorded for SIBs anode. Amorphous carbon materials that are generally obtained from the pyrolysis (T < 1500 °C) of hydrocarbon and organic polymer-based precursors that are divided into two groups, namely graphitizable (soft carbon) and non-graphitizable (hard carbon) carbons [59]. These types of carbons exhibit a structure bearing planar hexagonal layers with partial crosslinking of sp³ hybridized carbon atoms and area with graphitic-like structure bearing sp² carbon atom layers but lacking long-range order in the c direction (Fig. 4a,b) [59, 60]. Soft carbon is the one with reduced crosslinking as a result when these are subjected to heat treatment in the temperature range between 1500 to 3000 °C, the interlayer carbon atoms become mobilized and develop into graphite-like crystallites. While hard carbon has a high degree of crosslinking, therefore, their carbon layers remain immobilized even at high temperature and hence they will never transform towards a true graphitic structure [61]. Hard carbons receive their popular name as they are mechanically much harder in comparison to soft carbons. The degree of crosslinking is related to the accretion status of the transitional state achieved in the course of carbonization process as soft carbons are generally shaped from the fluid or gaseous state, unlike the hard carbon that originates from the solid phase. The general type of precursors used for hard carbon includes oxygen-rich organic materials, polymers such as phenol-formaldehyde resins together with plant-derived materials including cellulose, sugar, charcoal, and coconut shells etc. On the other hand, soft carbons are prepared from hydrocarbons and specifically aromatic based products [49]. The pyrolysis conditions and the composition of precursor play a primary role in the purity and yield of hard carbon. The two bands at 1350 (D-band) and 1580 cm⁻¹ (G-band) in Raman spectra demonstrate the varying degree of defect-induced mode and ordered graphitic mode, respectively. The degree of graphitization reduces when the rate of carbonization rises owing to increased relative order and the higher angle shift of (002) planes in XRD along with I_D/I_G ratio in Raman can provide and experimental evidence [62]. During carbonization process of hard carbon precursors the release of gases lead to materials with excellent properties like its exceptional porosity (1000 m² g⁻¹) [63], low particle density (1.4–1.8 g cm⁻³) [59, 64-66] low bulk powder density (0.35 g cm⁻³) [66], and the significant preservation of the initial polymeric microstructure.
Figure 4. A variety of schemes put forward by scientists in order to explain the actual design of hard carbon. Reproduced with permission [59, 60]. Copyright 2019 Royal Society of Chemistry.

Hard carbon is the most successfully used carbon anode for SIBs however there are numerous challenges related to their use. The precursor used for preparing hard carbon together with synthesis procedures, particle sizes, porosity, and vacancy defects plays an important role in achieving higher reversible capacities for SIBs. The first ever possibility of non-graphitic carbon as anode for SIBs was reported in 1993 where disordered soft carbon derived from pyrolysis of petroleum coke was used [51]. Later Stevens and Dahn explained the falling cards or house of cards mechanism of sodium storage in hard carbon [67-69]. According to which the first stage involves the addition of Na⁺ ions between the graphene layers causing an interlayer expansion resulting in the sloping voltage region as shown in Fig. 5a [69] followed by a second stage in which Na⁺ ion adsorb on the nanopores of the hard carbon structure producing a plateau region. The mechanism was named on cards due to the inherent structure of graphene layers placed one over the other like playing cards. The experimental evidence was provided by using small angle X-ray scattering (SAXS) where the diffraction peak shifts to lower 2θ suggesting an interlayer expansion of graphene layers (d-spacing = 3.8 Å) upon insertion of Na⁺ ions [70]. ²³Na NMR studies further revealed the sodiation mechanism in hard carbon where the two resonance peaks at 5.2 and 9.9 ppm are because of the presence of Na⁺ ion between the layers of hard carbon while a broader resonance peaks at about 9.0 and 16.0 ppm suggest the presence of Na⁺ ion in randomly distributed nanopores in hard carbon [71]. Templated carbon with hierarchical porosity with a pore volume of 0.798 cm³ g⁻¹ and an exposed surface of 346 m² g⁻¹ was developed by Wenzel et al., and found to present a superior rate capability of 100 mAh g⁻¹ at C/5 [72]. They also demonstrated the relationship between the electrochemical and physicochemical properties with commercially available high surface area (1041 m² g⁻¹) porous (1.008 cm³ g⁻¹ pore
volume) and non-porous carbon samples. They achieved improved capacity and rate performance unlike the high surface area commercial porous carbon, certifying that surface area and pore volume do not directly impact on increasing performance of SIBs anode [72]. Later some \textit{ab initio} studies have indicated that instead of increased interlayer distance the generation of vacancy defects in hard carbon helps increase the specific capacity by developing stronger binding with Na\textsuperscript{+} ions and overtaking the Van der Waal forces [73]. Bommier et al., later deviated from the card-house model by putting forward three-stage Na\textsuperscript{+} ions intercalation in hard carbon as shown in Fig. 5b. According to their study, the surface assembly of Na\textsuperscript{+} ions at defect bearing sites represented by the slope of the voltage region in Fig. 5b is followed by intercalation and finally adsorbed at the pore sites in hard carbon lattice during the plateau region [73, 74].

### 3.3 Graphene as anode for SIBs

To overcome the world energy demands, scientists are trying to regenerate the renewable resources. Rechargeable energy storage devices can be a surprise if their specific energy capacity and stability related problems get resolved. The unique structure of graphene makes it the ideal candidate for anode material in energy storage devices [75-80]. Graphene, as well as its modified forms like GO & rGO, are extensively utilized for SIB applications. Chou et al., first used graphene as an anode in SIBs in 2013 and achieved promising results [81]. Since then various composites of graphene, GO and rGO have been applied as promising anode for SIBs e.g., metal oxides graphene composites [82, 83].

![Graphene as anode for SIBs](image)

**Figure 5(a)** The voltage profile of glucose pyrolyzed to 1000 °C vs Na/Na\textsuperscript{+}; the details of the low-potential region are shown as an inset. Reproduced with permission [69]. Copyright 2019, Electrochemical Society

**Figure 5(b)** Visual representation of the card-house model on sodium-ion storage in hard carbon. The two distinct phases: pore filling and intercalation inside TNs are seen. Reproduced with permission [74] Copyright (2019) The American Chemical Society
Among various composites, SnO2 graphene composite showed very interesting properties due to their p-type nature, unidentified valence and large band gap for rechargeable energy storage devices [84-87]. SnO has a high theoretical capacity, large interlayer spacing and the layered morphology helps in minimizing the volumetric expansions during intercalation and de-intercalation. In this regard, Hang and coworkers fabricated 2D SnO anode that offers superior Na+ ion shuttling [88]. Present SnO electrodes, however, suffer from major capacity fading issues, mostly because of their volumetric changes, so various groups have opted carbon supports to composite the tin oxide (SnO) so to have better anode characteristics. The sluggish charge conduction issue of SnO can be mitigated by incorporating carbon cloth [89], carbon nanotubes (CNTs) [90], and graphene [90, 91]. Chen et al., [92] fabricated a flexible anode for SIBs composed of SnO nanoflake supported over 3D graphene/CNTs. Ultimately the 3D graphene/CNTs@SnO2 showed high rate performance and excellent steadiness during repeated cycling. When subjected to current rates starting from 100 to 1000 mA g\(^{-1}\), the resulting specific capacity of the graphene/CNTs@SnO2 declined from 584 to 390 mA g\(^{-1}\), respectively.

In continuation of this work on metal oxide/graphene composites various transition metals have been used as bare or composited to make them compatible in energy storage application. In 2014, Jian et al., [82] fabricated Fe2O3/GNS for SIBs which showed cycling performance of 400 mAh g\(^{-1}\) (100 mA g\(^{-1}\)) above 200 cycles. Because of its suitable theoretical capacity, the ferric oxide is also being considered as potential electrode material for SIBs, because of its natural abundance, low processing cost and non-toxicity but for practical application in energy storage devices the volume expansion, particle agglomeration and capacity fading issue must be mitigated [93-98]. To overcome the former issues making composites with carbonaceous material like graphene, porous carbon and CNTs may be a good addition. GO/rGO@Fe2O3 with different composite ratios exhibited promising electrochemical results.

Among other transition metals, CuO has gathered much attention principally due to its chemical stability, nontoxic nature, abundant sources and its low cost. CuO has undergone through many for its affability as an anode in secondary batteries [99]. However, due to high volume expansion and low conductivity, CuO is not suitable for SIBs. To eliminate these problems Klein et al., proposed a conversion type reaction for CuO in SIBs including building composites, optimizing nanoparticles structure and tough architecture [99-103]. Wang et al., reported an electrospinning technique to synthesize CuO quantum dots which were wrapped in carbon nanofibers. They utilized it as binder-free SIB anode achieving higher gravimetric capacity. Similarly, rGO with excellent electrical and robust mechanical flexibility was incorporated into CuO anodes. The
synergistic effect of CuO and rGO is ascertained from the high performance of CuO/rGO composite ranging from 470 (100 mA g\(^{-1}\)) to 350 mAh g\(^{-1}\) (2000 mA g\(^{-1}\)) [104].

Due to the suitable theoretical capacity of 718 mAh g\(^{-1}\), abundance and eco-friendly nature, NiO is one of the most well-known anode materials for SIBs. The drawback of NiO is the sluggish Na\(^+\) ion kinetics offered by the NiO and high particle agglomeration produced by volume changes that lead to irreversible capacity fading and lower cyclic stability issues [105]. Electrochemical properties of NiO for SIBs are even not seen in some cases [106]. He et al., [107] followed mechanistic approach using a series of correlated techniques like synchrotron studies, real-time electron spectroscopy and X-ray diffraction to observe stepwise reaction products and it was found that NiO continuously gets transformed into Ni and Na\(_2\)O when bond with Na\(^+\). A NiO/NiO-graphene hybrid fabricated from a Ni derived MOF (metal organic framework) has been utilized that offered high capacity as SIB anode [108]. As displayed in Fig. 6a-d, the cycle stability of the NiO/Ni/graphene anode was highly favorable with low fading capacities (0.2% / cycle) and the rate capabilities reported at 0.2, 0.5, 1 and 2 A g\(^{-1}\) were respective of 295, 385, 207 and 248 mAh g\(^{-1}\).

Various reports suggest the possibility of CoO as a potential substitute for the graphite anode of LIBs mainly because of its modest theoretical capacity (715 mAh g\(^{-1}\)) [109] but its applicability for the SIBs has not been much reported [110]. Chang et al., revealed a low-temperature fabrication of CoO microsphere films on to a Cu foil with an effective surface area of 103 m\(^2\) g\(^{-1}\) using a hydrothermal method. As an anode for SIBs, these CoO microspheres exhibited a capacity of 172 mAh g\(^{-1}\) (100 mA g\(^{-1}\)) at 100\(^{th}\) cycle [111]. In order to mitigate the problems of large volumetric changes and enhancing the electrical conductivity, composites with graphene can provide positive solutions to these drawbacks.

Titanium dioxide (TiO\(_2\)) has proved itself a versatile candidate with applications in photocatalysis, fuel cells and batteries etc. undoubtedly because of its nontoxic nature, abundant resources, cost-effectiveness and exceptional stability. TiO\(_2\) has already been proven an effective electrode for SIBs and has various phases such as anatase, brookite, rutile and hollandite [112, 113]. Owing to different structures TiO\(_2\) can offer excellent stable capacities when utilized as anode for SIBs in its various polymorphs mainly anatase, rutile and brookite. Anatase has been reported to be more favoured and can offer 2D diffusion channels for Na\(^+\) ion insertion [114]. But the main problem for TiO\(_2\) as anode for SIBs belong to its low conductivity, sluggish kinetics for Na\(^+\), low capacity with large capacity loss, especially at higher current densities. These problems can be minimized by forming composites, heteroatom doping and combination with
carbonaceous materials. Generally, CNTs, porous carbon and graphene are regarded as superior additive [115, 116].

Due to its well renowned electrical conductivity, price compatibility and high chemical stabilization, MoO$_2$ has gained more attention among various transition metals and has exhibited promising results as an electrode for SIBs [117, 118]. But MoO$_2$ is not an upright candidate for energy storage devices owing to volume expansion problem. Many trials are being carried out to overcome this issue especially by applying conductive carbon coatings to prevent volume expansion beyond a certain limit [119, 120]. Huang et al., investigated MoO$_2$/GO composite for SIB anode that is capable to deliver a gravimetric capacity of 483 mAh g$^{-1}$ (100 mA g$^{-1}$) at 10$^{th}$ cycle [120].

Figure 6. (a) Cyclic voltammogram curves for first three cycles of NiO/Ni/Graphene composite vs Na/Na$^+$ (b) Voltage profile of NiO/Ni/Graphene composite vs Na/Na$^+$ for selected cycles at different current densities. (c) Cyclic charge-discharge performance of NiO/Ni/Graphene composite with corresponding columbic efficiencies. (d) Rate performance of NiO/Ni/Graphene composite at various current densities. Reproduced with permission [108], Copyright 2019 The American Chemical Society.
VO₂ is yet another transition metal oxide much explored for being a potential anodic material in LIBs whereby it offers high capacity while being abundant in sources with low cost, however for SIB anode its results are not so impressive especially as anode [121]. Man thiram et al., [122] investigated electrochemical properties of VO₂/rGO in energy storage systems however, owing to the large particle size of VO₂ higher capacities were not achieved. More studies are required to understand the reaction mechanism at low potential regions. Due to its layered structure, V₂O₅ is commonly used as a catalyst and in power storage devices [123-127]. The intercalating distance of orthorhombic V₂O₅ (4.37 Å) is not considered suitable for SIBs as owing to layer type its capacity fades rapidly [128]. Moretti’s group first time investigated the use of amorphous V₂O₅ as anode for SIBs. To increase the cycle stability, rate capacity and electronic conductivity GO/rGO can be used as an additive. Only a few results have been reported as cathode for SIBs using V₂O₅/graphene composite [128, 129].

Transition metal dichalcogenides, especially metal sulfides, have recently gained researchers interest with their distinctive physicochemical characteristics and potential applications in energy storage devices [130, 131]. WS₂/graphene nanocomposites fabricated via simple hydrothermal process [132] have been used as an anode in SIBs exhibiting the reversible specific capacity of 594 mAh g⁻¹ and after 500 cycles 283 mAh g⁻¹ (40 mA g⁻¹) capacity was still retained. The proposed electrochemical reaction may be as,

\[ \text{MS}_2 + \text{Na}^+ + \text{e}^- \leftrightarrow \text{M} + \text{NaS}_2 \quad (\text{M} = \text{Ni, W}) \quad (\text{Eq.2}) \]

In 2014, various investigations have been carried out into MoS₂/rGO nanocomposites. The exfoliated MoS₂/rGO composite revealed a specific capacity of 165 mAh g⁻¹ at the end of the 50th cycle under 20 mA g⁻¹ current rate [133].

In the preparation of SbOₓ/rGO composite, Zhou et al., [134] used wet ball milling technique and it delivered 352 mAh g⁻¹ (5 A g⁻¹) capacity at 100th cycle, while 409 mAh g⁻¹ capacity is offered while using current density of 1 A g⁻¹, with more than 95% retention in capacity for SIB. Similarly, Sb₂S₃/rGO composite based SIB anodes were investigated offering 700 mAh g⁻¹ at 0.05 A g⁻¹ with smaller capacity fading till the end of 50 cycles [135]. The following reactions were proposed to be taking place,

\[ \text{Sb}_2\text{S}_3 + 6\text{Na}^+ + 6\text{e}^- \leftrightarrow 2\text{Sb} + 3\text{Na}_2\text{S} \quad (\text{Eq.3}) \]
Sulphides have been opted as SIB anode because of their suitably higher capacity, natural abundance and economy. But unfortunately, their sodium intercalating mechanism controlled fabrication and cycling performance still matters of concern.

3.4 Carbon nanofibers as anode for SIBs

Carbon nanofibers belong to 1D (one-dimensional) carbon-based materials consisting of discontinuous cylindrical filaments having aspect ratios greater than 100. They contain sp²-hybridized carbon atoms but differ from CNTs as they do not have graphene layers [136-138]. Carbon nanofibers possess excellent electronic conductivity making them well suited for applications as an electrode for both LIBs and SIBs to enhance their electrochemical performance. Carbon nanofibers have been structured by several synthetic protocols including electrospinning, catalytic chemical vapour deposition growth, biomass methods and template-based synthesis [139-145].

ID carbon nanofibers that are synthesized from cracking of polymers display encouraging electrochemical performance as SIBs anode due to the abundance of defect sites for Na⁺ ion storage [146-159]. To see the effect of porous morphology Li et al., used Pluronic F-127, a triblock copolymer as a precursor to synthesize porous carbon nanofibers that were found to be highly effective as SIB anode [148]. As shown in Fig. 7a,b the porous carbon fibre shows a good rate capability of 60 mAh g⁻¹ (10,000 mA g⁻¹) with an excellent reversible capacity of 266 mAh g⁻¹ when cycled at 50 mA g⁻¹ current density. These distinctive results have been credited to the 3D interconnected microspores that not only increase the surface available for a reaction but also increase the structural stability during cycling to prevent any cracking. Motivated by this work, several other efforts have been carried out to synthesize porous carbon nanofibers together with nitrogen and/or oxygen doping to induce defects to increase ion-storage sites. For this purpose, usually, some rich nitrogen-containing polymers (e.g. polyamide, polypyrrole) is used and subjected to carbonization to induce pores during decomposition and possible heteroatom doping [146, 152, 154, 156-158]. A practical example is a preparation of dual doped porous carbon nanofiber that is prepared from the breakdown of bacterial cellulose and polyaniline [160]. The porous cellulose@PANI nanofibers based material presents 545 mAh g⁻¹ (100 mA g⁻¹) capacity after 100 cycles with improved rate performance. The high reversible capacity is ascribed to 3D interconnected pores and heteroatom doping that can together enhance electronic conductivity, penetration of electrolyte, fast electron transfer pathway and increased storage sites.
Figure 7. (a) Cyclic charge-discharge performance of P-CNFs for 100 cycles at 50 mA g\(^{-1}\) and (b) Rate capability of P-CNFs at various current densities. Reproduced with permission, [147] Copyright 2019 Royal Society of Chemistry.

Other than fabricating various morphologies of carbon nanofibers, scientists have attempted to prepare nanocomposite structures to get more benefited from the capabilities of carbon nanofibers as anode for SIBs. Using both outer surface anchoring and encapsulation methodologies various carbon nanofiber based composites are reported. Hou et al., prepared polypyrrole derived carbon nanofiber that was decorated with Sb nanoparticles to tune up the surface of carbon nanofiber [143]. An improved cycling performance with a capacity retention of 96.7% was observed when the materials electrode was cycled at 100 mA g\(^{-1}\) for 100 cycles. When the materials electrode was cycled at a current density of 100 mA g\(^{-1}\) for 100 cycles an improved cycling performance with a capacity retention of 96.7% was observed. In order to circumvent the huge volume changes of Sb, an encapsulation strategy was proposed by Zhu et al., and they prepared 0.4 nm thick MoS\(_2\) nanoplates that were encapsulated in carbon nanofiber [161]. They noticed an increased reversible capacity of up to 484 mAh g\(^{-1}\) at a moderately low current of 1000 mA g\(^{-1}\) and 253 mAh g\(^{-1}\) even at a very high rate of 10,000 mA g\(^{-1}\). Various researchers have adopted similar strategy using other metal oxides, sulfides and selenides such as Li\(_4\)Ti\(_5\)O\(_{12}\) [162], SnO\(_2\) [163], MnFe\(_2\)O\(_4\) [164], TiO\(_2\) [115], MoS\(_2\) [165, 166], FeSe\(_2\) [167], and NiSe\(_2\) [168] for improving electronic and ionic conductivities also adopt an almost similar strategy. Later, porous carbon nanofibers bearing electrodeposited SnO\(_2\) with carbon coating (PCNF@SnO\(_2\)@C) was also applied as composite carbon fibre anode for SIBs and the results were quite impressive with the high storage capability of 374 mAh g\(^{-1}\) up to 100 cycles at 50 mA g\(^{-1}\) of current density.
and high rate capability [169]. The reason for this electrochemical activity was attributed to the porous and elastic nature of carbon nanofibers and protective effect of the carbon coating layer together with SnO₂ as active redox metal. There are numerous other research articles highlighting the benefits of porous carbon nanofibers, doping with some heteroatom, surface anchoring with metals and encapsulation structures for the enhancement of structural feature that can ultimately effect sodium storage performance as displayed in Table 2 [146, 148, 149, 151-154, 156-158, 170] and Table 3 [58, 115, 143, 161, 171-181].

Table 2  List of reported carbon nanofibers based anodes for SIBs. Reproduced with permission [138]. Copyright 2019 Royal Society of Chemistry

<table>
<thead>
<tr>
<th>Materials</th>
<th>Preparation strategy</th>
<th>Diameter &amp; Surface area</th>
<th>Electrochemical performance (mAh g⁻¹)</th>
<th>Rate (mA g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNFs</td>
<td>Biomass method</td>
<td>50 ~ 100 nm / 377 m² g⁻¹</td>
<td>176 after 600 cycles</td>
<td>200</td>
</tr>
<tr>
<td>CNFs</td>
<td>Electrospinning</td>
<td>200 ~ 300 nm / NA</td>
<td>233</td>
<td>50</td>
</tr>
<tr>
<td>Porous CNFs</td>
<td>Electrospinning, F127 template</td>
<td>~280 nm / 74.59 m² g⁻¹</td>
<td>266 after 100 cycles</td>
<td>50</td>
</tr>
<tr>
<td>CNFs@N-doped porous carbon</td>
<td>Biomass (CNFs), Oxidative template assembly (porous carbon)</td>
<td>80 ~ 110 nm / 300.2 m² g⁻¹</td>
<td>240 after 100 cycles</td>
<td>100</td>
</tr>
<tr>
<td>N-doped porous CNFs</td>
<td>Oxidative template assembly</td>
<td>50 ~ 70 nm / 1508 m² g⁻¹</td>
<td>243 after 100 cycles</td>
<td>50</td>
</tr>
<tr>
<td>N-doped CNFs</td>
<td>Electrospinning</td>
<td>100 ~ 300 nm / 564.4 m² g⁻¹</td>
<td>377 after 100 cycles</td>
<td>100</td>
</tr>
<tr>
<td>N-doped hollow CNFs</td>
<td>Oxidative template assembly, KOH activation</td>
<td>~300 nm / 868 m² g⁻¹</td>
<td>160 after 100 cycles</td>
<td>50</td>
</tr>
<tr>
<td>N-doped CNFs</td>
<td>Electrospinning, N2 treatment</td>
<td>~150 nm / 513.89 m² g⁻¹</td>
<td>254 after 100 cycles</td>
<td>50</td>
</tr>
<tr>
<td>N-doped CNFs</td>
<td>Electrospinning, urea treatment</td>
<td>~250 nm / 8.16 m² g⁻¹</td>
<td>354 after 100 cycles</td>
<td>50</td>
</tr>
<tr>
<td>N, O-doped porous CNFs</td>
<td>Biomass (CNFs), Oxidative template assembly (porous carbon), KOH activation</td>
<td>100 ~ 150 nm / 1426.1 m² g⁻¹</td>
<td>545 after 100 cycles</td>
<td>100</td>
</tr>
<tr>
<td>N, B-doped porous CNFs</td>
<td>Biomass (CNFs), NH₄HB₄O₇·H₂O treatment</td>
<td>30 ~ 80 nm / 1585 m² g⁻¹</td>
<td>581 after 120 cycles</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 3  List of reported carbon nanofibers based composite anodes for SIBs. Reproduced with permission [138]. Copyright 2019 Royal Society of Chemistry

<table>
<thead>
<tr>
<th>Materials</th>
<th>Preparation strategy</th>
<th>Diameter &amp; Surface area</th>
<th>Active material &amp; Weight Content</th>
<th>Electrochemical performance (mAh g⁻¹)</th>
<th>Rate (mA g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb anchored on CNFs</td>
<td>Biomass method (CNFs), Solution method (Sb)</td>
<td>~50 nm / 160.3 m² g⁻¹</td>
<td>Sb, 80.8 wt%</td>
<td>542.5 after 100 cycles</td>
<td>100</td>
</tr>
<tr>
<td>PCNF@SnO2@C</td>
<td>Electrospinning (CNFs), Electrodeposition (SnO₂), CVD (carbon coating layer)</td>
<td>~200 nm / N/A</td>
<td>SnO₂, 38.5 wt%</td>
<td>374 after 100 cycles</td>
<td>50</td>
</tr>
<tr>
<td>Sb@CNFs</td>
<td>Electrospinning</td>
<td>~200 nm / N/A</td>
<td>Sb, 38 wt%</td>
<td>446 after 400 cycles</td>
<td>200</td>
</tr>
<tr>
<td>Sb@CNFs</td>
<td>Electrospinning</td>
<td>~250 nm / N/A</td>
<td>Sb, 54 wt%</td>
<td>350 after 300 cycles</td>
<td>100</td>
</tr>
</tbody>
</table>
3.5 Biomass-derived carbon as anode for SIBs

Biomass is an organic material mainly composed of C, H and O. After burning process of biomass the derived carbon can be a useful raw material for SIBs anode. Usually, carbon obtained from biomass has an amorphous structure which is more suitable for batteries due to its low production cost and easy synthesis process [182-185]. Biomass-derived carbon resources are found abundantly and eco-friendly, so these are attracting considerable attention towards them. Biomass carbon is commonly obtained through followings steps (a) washing, (b) drying to remove moisture, (c) calcination at elevated temperature. Previously, a diversity of carbonaceous materials have been obtained through biomass and used in storage devices [186]. Carbonaceous material obtained through carbonization of woods have current collector free and binder free properties [183]. Ding et al., [182] fabricated less graphitic carbon nanosheets micropores frameworks possessing a wider distance between the layers (0.388 nm) as compared to that for ordered graphite (0.335 nm). When applied as an anode in SIB the insertion and deinsertion capability of Na⁺ ion is 306 and 532 mAh g⁻¹ at varying current densities. While at a current of 100 mA g⁻¹ the sodium storing capacity dropped to 255 mAh g⁻¹ upon extended cycling of up to 200. Mitlin et al., [187] obtained carbon from banana peels that have a lesser surface area and this material showed 336 mAh g⁻¹ as capacity with 11% drop in capacity after repeatedly undergoing 300 cycles of charge and discharge. At low current density 500 mA g⁻¹ the achievable gravimetric capacity is 221 mAh g⁻¹ and after cycling it merely reduces by 7%. Yang and co-workers [184] obtained
N-doped carbon from okra through carbonization and exfoliated the sheets to get the high specific area with facile sodiation and desodiation into carbon sheets during cycling. The remarkably high surface area yielded a capacity of 292.2 mAh g\(^{-1}\) with a steady C.E for more than 2000 cycles. Hu et al., [188] demonstrated various biomass-derived hard carbon-based potential materials for SIBs anode. Similarly, it is reported that the hard carbon-based micro tubes derived from carbonization of natural carbon at 1000, 1300, and 1600 °C are capable to offer a temperature dependent, sufficiently high SIB anode performance. The electrochemical activity has also increased with an increase in the temperatures of carbonization from 1000, 1300 to 1600 °C, demonstrating that the electrochemistry is seriously linked to the carbonizing temperature of the hard carbon microtubes [189]. Apple waste derived hard carbonaceous anode material [190] showed high SIB performance and has the advantage of incorporation of nitrogen and sulfur from apple proteins, that assists sodiation and desodiation reactions.

Zhao et al., [191] presented carbon nanoparticles derived from the flame deposition of coconut oil and demonstrated a second cycle sodiation and desodiation capacities of 277 and 217 mAh g\(^{-1}\) at 100 mA g\(^{-1}\) after 20 cycles. Doped carbon microsphere were also produced through carbonization from oatmeal [192]. The electrochemical results showed that after 50 cycles N-doped carbon microsphere delivered a capacity of 336 mAh g\(^{-1}\) when cycled at 50 mA g\(^{-1}\) current. Huang et al., [185] described a hard carbon SIB anode material derived from pomelo peels by pyrolizing in H\(_3\)PO\(_4\) to yield a high surface area hard carbon containing O/P containing functional groups that can show a pseudocapacitive effect from exterior redox reaction. After 220 cycles the reversible capacity of SIBs remained 181 mAh g\(^{-1}\) (200 mA g\(^{-1}\)) but, regrettably, the initial C.E of the material was only 27%. Hu et al. [193] suggested a single stage heat treatment to get carbon sheath from natural leaves and showed promising electrochemical performances with a large first C.E of 74.8% together with a high reversible capacity of 360 mAh g\(^{-1}\) (Fig. 8a-i). Li and coworkers [183] fabricated an ultra-thin mesoporous carbon by simple carbonization of wood and the as-synthesized mesoporous carbon had well-aligned pores in the horizontal and vertical directions. In SIBs, mesoporous carbon is proposed to be applied with high outcomes in terms of capacity (13.6 mAg cm\(^{-3}\)) which is greater than that for orthodox LIBs together with benefits of being binder and current collector free anode. Zheng et al., [194] fabricated a dual-natured hard carbon by hydrothermal and subsequent pyrolytic treatment of holly leaf and the resulting carbon possess both mesopores and macropores with tiny stranded graphitic domains. It has been proposed that the hydrothermal treatment is vital for the lamella-like structuring and enlarged pores along with nanoporous graphitic portions obtained directly by pyrolyzing the holly leaves. Lamellar fabricated carbon showed the high sodium storage of 318 mAh g\(^{-1}\) (20 mA g\(^{-1}\))
with superb rate performance. It is worth to conclude that to choose the biomass precursor consideration should be made that it must not be obtained from highly consumed food to avoid its scarcity and price issues. It should be significant that biomass contains unique chemical composition and microstructure which may directly define the composition and structure of obtained carbonaceous material, most importantly electrochemical features of sodium storage performances [195].

3.6 Heteroatom-doped carbon materials as anode for SIBs

Heteroatom doped (e.g. N, S, P and B) carbon anode materials have been explored for SIBs and have proved to boost the capacity, electronic wettability and electronic conductivity which can ease the electrode/electrolyte interactions and charge transfer [196, 197]. Thus, various heteroatom based carbonaceous materials have come up with improved performance as conceivable anodes for SIBs while noteworthy results have been shown by some candidates. So far, N-doped carbon anodic materials have come up with great potential that enhances the electronic conductivity and reaction activity by producing extrinsic imperfections. Huang et al., [198] in 2013, reported carbon nanofiber doped with nitrogen showing 134 mAh g⁻¹ reversible capacity after 200 cycles at 0.2 A g⁻¹ while the anodic material has been shown to deliver a 72 mAh g⁻¹ capacity at a current of 20 A g⁻¹. Afterwards, a number of carbon-based materials with different morphologies have been doped with nitrogen for enhanced performance as SIBs anode. For instance, porous carbon-based nanosheets, mesoporous carbon, carbon films, CNTs and carbon spheres with N-doping have been reported in addition to the various graphene-based anodes with nitrogen doping, etc. [146, 158, 196-200]. From these 3d graphene foams [197] doped with nitrogen have shown a higher N-content of 6.8 % displaying a capacity of 1057.1 mAh g⁻¹ (0.1 A g⁻¹) and 594 mAh g⁻¹ (150 A g⁻¹). They have also explored rGO and GO-based nitrogen doped anode for SIBs with improved sodiation capacity and they proposed that the synergistic effect of 3d foam like morphology and N-doping impart role in improving the electrochemical cycling behaviour of the electrodes. Lou et al. [154] found that after extending their cycling up to 7000 cycles, the reversible storage capacities of free-standing carbon nanofiber films doped with nitrogen (7.15 wt%) were around 210 mAh g⁻¹ at 15 mA g⁻¹ while at the higher current rate of 5000 mA g⁻¹ it was still maintained at a level of 154 mAh g⁻¹. The cyclic capability has been designated to high mechanical flexibility with improved structural stability.

Recent attempts to improve the reversible sodium ion capacity by using sulfur-doped carbonaceous anodes have also proved somewhat fruitful. Furthermore, the introduction of S can increase the intercalating distance between the layers which not only increases
capacity but the speed of Na\(^+\) intercalation/de-intercalation. Therefore, S-doping may significantly enhance sodium storage characteristics of carbonaceous material. Chen et al. [201] have outlined the electrochemical features of sulfur covalently linked to graphene with the specific sodium storage capability of 291 mAh g\(^{-1}\) (0.05 A g\(^{-1}\)) and outstanding durability after 200 continuous cycles. Jiang et al., [202] discovered Na storage performance of S-doped disarranged carbon with 26.91% sulfur concentration achieved by pyrolizing sulfur and NTCDA (1,4,5,8-Naphthalenetetracarboxylic dianhydride). The maximum sodium storage of 516 mAh g\(^{-1}\) (20 mA g\(^{-1}\)) and 271 mAh g\(^{-1}\) (1000 mA g\(^{-1}\)) was achieved upon 1000 cycles corresponding to capacity maintenance of 85.9% (Fig. 9a-c). Similarly, the effect of sulfur doping on carbon as a function of sodium storage performance has also been found by Huang et al., [203]. The resulting doped material with a 15.17 wt% sulfur revealed a wider 0.386 nm interlayer spacing showing an elevated capacity of 303.2 mAh g\(^{-1}\) (500 mA g\(^{-1}\)) and a high C.E of 73.6% after 700 cycles.

Similarly, The phosphorous doped carbon nanosheets as SIB anode holding a capacity of 328 mAh g\(^{-1}\) (100 mA g\(^{-1}\)) have been reported with wider interplanar distance of 0.42 nm [204] and after 5000 cycles it is fascinating to observe that the as-doped material presented a storage competence of up to 149 mAh g\(^{-1}\) (5 A g\(^{-1}\)). This prominent efficiency behaviour is credited to the following arguments: a) smaller Na\(^+\) path length and more active sites produced from owing to the ultrathin nanosheets accompanied with large surface area, b) the proficient intercalating distance which can ease the insertion/de-insertion of Na\(^+\), c) transformation of the electronic states upon doping that also facilitate the adsorption of ions in the electrolyte.

Boron came up as a significant dopant for the carbonaceous anode in SIB applications, particularly of its similarity in size with carbon, along with lower electronegativity. Wang's group [205] reported the role of boron as a linker with the oxygen that helps in the expansion of the intercalating distance in the rGO along with the generation of defects that promote the sodium ion storage ability of rGO. As anticipated the rGO incorporated with boron produced 280 mAh g\(^{-1}\) (0.02 mA g\(^{-1}\)) capacity that is greater as compared to bare rGO matching nicely with the outcomes of the results reported by Mizuno and Ling [206]. Furthermore, as a next step, various groups have exploited the effect of doping of more than one heteroatoms to revive the sodiation capacity of the carbon-based anodes. To additionally increase the properties of carbon both N, S- and N, P-codoping were fabricated as N-doping alone improves the electronic conductivity and S or P-doping alone can affect the gaps between the layers of carbon. Zhang et al., [207] fabricated graded nitrogen and sulfur co-doped carbon nanospheres by pyrolysis of polyaniline and cellulose which exhibited a steady 3400 electrochemical cycles displaying a sodium
storage capacity of 150 mAh g\(^{-1}\) which is substantially superior to S-doped carbon microsphere, bare and N-doped carbon sphere. Zhou and coworkers [208] used a gas-solid phase synthetic approach to replace nitrogen atoms from the doped nitrogen-rich carbon by sulfur atoms and noted the efficiency of this codoped material for SIB anode. The incorporation of the sulfur has a prominent effect on the carbon matrix producing large specific area, distorted structure and greater interlayer distance. Moreover, they used DFT calculations to show the S-doping influence, revealing that computed d-spacing of N-C and S-N/C are 3.47 and 3.73 Å, respectively. The N-doped carbon and S/N-codoped cyclic voltammetry curves show a pair of other redox spikes (1.85/1.05 V) that are unlike the Na\(^+\) battery, showing that during the Na\(^+\) intercalation/deintercalation process the C-S-C-bonds are not reconstructing and broken and the capacity may be partially enhanced by the Faradaic reaction between S and Na\(^+\) ions that are associated with carbon. S/N co-doped carbon improved electrochemical behaviour and they can deliver a capacity of 350 mAh g\(^{-1}\) (500 mA g\(^{-1}\)) and 110 mAh g\(^{-1}\) (10,000 mA g\(^{-1}\)), respectively in SIB.

Li et al., [209] fabricated a P/N-codoped carbon microsphere using the solvothermal process and checked its activity as SIB anode. Their results showed the exceptional sodium storing capacity of the N/P-codoped carbon electrode with the sodium storage capability of 305 mAh g\(^{-1}\) (100 mA g\(^{-1}\)) and 136 mAh g\(^{-1}\) (5000 mA g\(^{-1}\)). N/O-codoped carbon network was fabricated by Yu and co-workers [149] by thermally blending a mixture of bacteria-contaminated cellulose and polyaniline through KOH. The interlinked carbon nanofibrous network is able to facilitate the electron passage through channels and intensive nanopores in the carbon nanofibers can make available a number of lively spots for storing more sodium ions. The co-doping of N and O would improve the surface wettability and electrical conductivity of anode material based on carbon. Furthermore, it facilitates the contact between the electrode and the electrolyte and reduces the propagation range of Na\(^+\) with its wonderful 3D carbon framework and large available surface. The NOC (N/O codoped carbon) demonstrated outstanding sodium storage characteristics with elevated capacities and cycle stabilization taking advantage of these properties. A stable capacity of 545 mAh g\(^{-1}\) (100 mA g\(^{-1}\)) was maintained at 100\(^{th}\) cycle along with a nominal capacity of 240 mAh g\(^{-1}\) (2000 mA g\(^{-1}\)) after 2000 cycles.

References


[46] X. Li, X. Li, L. Fan, Z. Yu, B. Yan, D. Xiong, X. Song, S. Li, K.R. Adair, D. Li, Rational design of Sn/SnO2/porous carbon nanocomposites as anode materials for


[58] Y. Liu, N. Zhang, C. Yu, L. Jiao, J. Chen, MnFe$_2$O$_4$@C nanofibers as high-performance anode for sodium-ion batteries, Nano Lett. 16 (2016) 3321-3328. https://doi.org/10.1021/acs.nanolett.6b00942


[85] H. Yamaguchi, S. Nakanishi, H. Iba, T. Itoh, Amorphous polymeric anode materials from poly (acrylic acid) and tin (II) oxide for lithium ion batteries, J. Power Sources 275 (2015) 1-5. https://doi.org/10.1016/j.jpowsour.2014.10.071


[152] Z. Zhang, J. Zhang, X. Zhao, F. Yang, Core-sheath structured porous carbon nanofiber composite anode material derived from bacterial cellulose/polypyrrole as an anode for sodium-ion batteries, Carbon 95 (2015) 552-559. https://doi.org/10.1016/j.carbon.2015.08.069


[164] Y. Liu, N. Zhang, C. Yu, L. Jiao, J. Chen, MnFe$_2$O$_4$@C nanofibers as high-performance anode for sodium-ion batteries, Nano Lett. 16 (2016) 3321-3328. https://doi.org/10.1021/acs.nanolett.6b00942


