



Optimizing nitrogen doping strategies in hard carbon for enhanced performance in sodium-ion batteries

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ABSTRACT

Sodium-ion batteries are emerging as a promising and cost-effective alternative to lithium-ion batteries for large-scale applications. Among various anode materials, hard carbon has become a preferred choice for sodium-ion batteries. This study focuses on synthesizing hard carbon from bio-waste cherries and investigating the impact of nitrogen doping strategies on its electrochemical performance. Using urea as a precursor, post nitrogen doping was found to enhance the structural properties of hard carbon, facilitating better penetration of sodium ions into its internal structure. The results revealed that post nitrogen doping significantly improved the capacity of hard carbon, increasing it from 206 mAh g⁻¹ to 274 mAh g⁻¹ at a current density of 20 mA g⁻¹. Additionally, the post nitrogen-doped hard carbon demonstrated an impressive capacity of 110 mAh g⁻¹ at a high current density of 1 A g⁻¹. These findings underscore the potential of nitrogen doping in optimizing hard carbon for sodium-ion battery applications.

1. Introduction

Hard carbon, primarily characterized by sp-bonding, is a disordered carbon material that is neither graphitic nor capable of converting into graphite. It has a mixed-up structure with layers of graphene that are stacked but not arranged in a regular pattern, surrounded by a complicated network of carbon that includes tiny holes or very small pores [1–5]. Hard carbons are very hard because their building blocks are linked together in a way that stops them from forming a regular graphite structure [6,7]. The structure of hard carbon is made up of randomly shaped, curved graphene layers, which have different sizes between the layers, unlike graphite [8,9]. Due to this structure, hard carbon is suitable for the intercalation of sodium ions, which are larger than lithium ions. The pore size and interlayer distance that is present in hard carbon allows sodium ions to penetrate into the structure [1,3,10–13]. One of the main advantages of hard carbon is its precursors, which are extracted from biological waste such as fruit and berry seeds, wheat, coffee residues, eggshells and others. Thus, hard carbon contributes to the recycling of bio-waste and correlates with the sustainable

development goals outlined by the UN.

Hard carbon is synthesized by heating the carbon-containing precursor in an inert atmosphere with an absence of oxygen, which is called pyrolysis. The temperatures are usually higher than 1000°C and the heating rate is between 1 - 10°C min⁻¹. Increase in carbonization temperature favors formation of nanopores, which then increases specific capacity. However, this is only applicable for a certain range of carbonization temperatures (1000–1300°C) [14–19]. The formed HC's structure will depend on these temperatures and the precursor's initial structure. When selecting a precursor for the synthesis of hard carbon, it is important to take into account the content of carbon and its bonds in the structure of the material. Functional groups such as C=O, C=N, and C-H are responsible for the porosity and chaotic morphology of the resulting anode material [20]. The above-mentioned biowaste containing various organic compounds has a similar structure and high carbon content. According to Vassilev et al., biomass mainly consists of organic components like hemicellulose, lignin and cellulose [21]. There are a lot of research papers in which synthesis of hard carbon from various biomass precursors are discussed. Locust wood (382.3 mAh g⁻¹ at 0.1C),

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[22] shaddock peel 430.5 (at 0.03 A g⁻¹), [23] pinecone (370 mAh g⁻¹ at 0.03 A g⁻¹), [23] Prunus armeniaca (210.2 mAh g⁻¹ at 0.1 A g⁻¹) [24] and starch (239 mAh g⁻¹ at 0.1C) [25] are the examples of biomass from which HC was synthesized. The structure of HC and its electrochemical performance can be altered by several methods, such as washing the precursor, which positively affects cycling performance and increases specific capacity from 299 mAh g⁻¹ to 430.5 mAh g⁻¹ in the case of cone-derived HC [26]. Also, doping by heteroatoms like Boron (B), Phosphorus (P), Sulfur (S) and Nitrogen (N), can further affect electrochemical performance of the material and pre-oxidation that adds oxygen into the structure of the precursor [27–35].

In this work, nitrogen doping improved the electrochemical performance of waste-derived hard carbon. The study found that the optimal method for nitrogen doping was post-doping, which proved to be the most effective. The results show that nitrogen doping significantly increases the capacity of hard carbon, raising it from 206 mAh g⁻¹ to 274 mAh g⁻¹ at a current density of 20 mA g⁻¹. Additionally, the nitrogen-doped hard carbon demonstrated remarkable capacitance, reaching 110 mAh g⁻¹ at a current rate of 1 A g⁻¹. This evidence underscores the promise of nitrogen doping as a strategy for optimizing hard carbon in sodium-ion battery applications.

2. Experimental

2.1. Bio-waste treatment

The primary carbon precursor used in this study is cherry pits. The first step in processing the biomass involves washing the material with deionized water. To further remove impurities, the washed material is treated with a 1M hydrochloric acid solution. After leaching in the acid, the material is rinsed with deionized water until the pH reaches 7. The material is then dried in a drying oven at 80°C for 24 hours.

2.2. Synthesis of hard carbon and doping procedure

Carbonization of hard carbon is a thermal treatment process where partial decomposition of material proceeds in a non-oxidative environment. As an environment, the argon gas was used with a purity of 99.987%. The doping process is required to enrich the nitrogen content in hard carbon. The method of doping is solid-state mixing of a hard carbon precursor with a dopant agent. As a dopant, urea was selected. The weight ratio between hard carbon precursor and dopant agent is 1:5. The high amount of dopant agent was selected to maximize the nitrogen content. Synthesis of doped hard carbon proceeded in a tubular furnace; the material carbonized at temperatures of 800°C, 1000°C, 1200°C, 1400°C, and 1500°C, with a heating rate of 4°C min⁻¹ and a dwelling time of 3 h. The post-doping treatment was conducted after hard carbon synthesis; it was re-carbonized again with the doping agent at 1000°C with a heating rate of 4°C min⁻¹, and the dwelling time was 3 h. Since 1000°C temperature had the highest nitrogen content.

2.3. Electrode preparation

To prepare the electrode, synthesized hard carbon was ground in agate mortar until the material became a powder. The process of slurry preparation proceeded in two mortars. In the first mortar, hard carbon powder was mixed with acetylene black (AB, MTI Corporation) to enhance conductivity. The second mortar is required to conduct a dissolution process for the binding agent in an organic solvent. The binder that was used is polyvinylidene fluoride (PVDF, Solef 5130), and the solvent was N-methyl-2-pyrrolidone (NMP, Sigma Aldrich). After dissolving PVDF, a mixture of hard carbon and AB was added to the second mortar and stirred with a pestle until the suspension became homogeneous. The mass ratio of hard carbon, AB, and PVDF is 80:10:10. Prepared electrode slurry was placed on copper foil, and with a micrometer-adjustable film applicator (doctor blade), the smooth film

was obtained. The thickness of the film was set to 25 microns on the doctor blade. After the application of the film, the electrode dried in a drying oven at 60°C.

2.4. Coin cell assembling

The battery assembly process was performed using a CR2032 coin cell configuration. The electrode discs were fabricated by punching the active material into circular shapes and carefully placing them into the lower casing of the coin cell. A separator composed of Absorbed Glass Mat (AGM) was positioned on top of the electrode disc, followed by the precise addition of 200 µL of electrolyte. The electrolyte consisted of 1 M NaPF₆ dissolved in a solvent mixture of ethylene carbonate (EC), dimethyl carbonate (DMC), and fluoroethylene carbonate (FEC) in a volume ratio of 49:49:2. A thin disc of sodium metal, prepared by mechanically rolling and cutting sodium metal, was placed atop the separator to serve as the counter electrode. The cell was then sealed by installing the cap and crimping it using a coin cell crimping machine. To ensure optimal conditions, all assembly steps were conducted within an argon-filled glove box, maintaining an atmosphere purity of 99.999% to prevent any contamination by moisture or oxygen.

2.5. Material characterization

X-ray diffraction (XRD) analysis was done on an X-ray Diffraction (XRD) System - SmartLab (Rigaku), in order to identify the interplanar spacing of material. The Raman spectroscopy LabRAM (Horiba) was used to study the graphitization degree of material, the used wavelength of the laser beam was 514.5 nm. The surface morphology of the material was examined by scanning electron microscope (SEM) ZEISS Crossbeam 540, and the internal structure was studied by transmission electron microscope (TEM) JEOL JEM - 1400 Plus. A galvanostatic charge-discharge test was conducted to identify the electrochemical performance of the electrode on the WonATech WBCS3000Ls32 battery test system.

3. Results and discussion

3.1. Morphology analysis by SEM and TEM

The morphology of materials was examined via SEM and TEM analysis. Figures 1a-f represented the surface morphology of bare hard carbon that carbonized at 1000°C, 1200°C, and 1400°C. Material structure is not uniform and has irregular shapes. Based on Figure 1, on a macro scale, material has pores and cavities with a diameter in a range of 5-20 micrometers. The cavities are filled with small, hard carbon particles; the appearance of small particles is the result of material crushing during the grinding process. On the microscale, the material has pores with diameters from 1 to 0.4 micrometers. The macrostructure and microstructure remained unaffected by the heating temperature.

The structural morphology of the material was examined by TEM. In Figure 2, a TEM image of bare hard carbon carbonized at 1000°C, 1200°C, and 1400°C is illustrated. Based on the results, at 1000°C, the amorphous structure and disordered pattern of carbon sheets (Figure 2 a,b), and no pseudo-graphitic structure was observed. At a temperature of 1200°C, it was observed that carbon sheets aligned and stacked together by creating a pseudo-graphitic structure (Figure 2c,d). At 1400°C the length of aligned carbon sheets is increased, and the number of pseudographitic domains becomes higher (Figure 2 e,f).

3.2. XRD analysis of hard carbon

XRD analysis was done for hard carbon at temperature range 800°C, 1000°C, 1200°C, 1400°C and 1000°C post-doped (Figure 3a). XRD pattern of hard carbon has wide low peaks that indicate the amorphous structure of the material. The peak that appears at 22° corresponds to

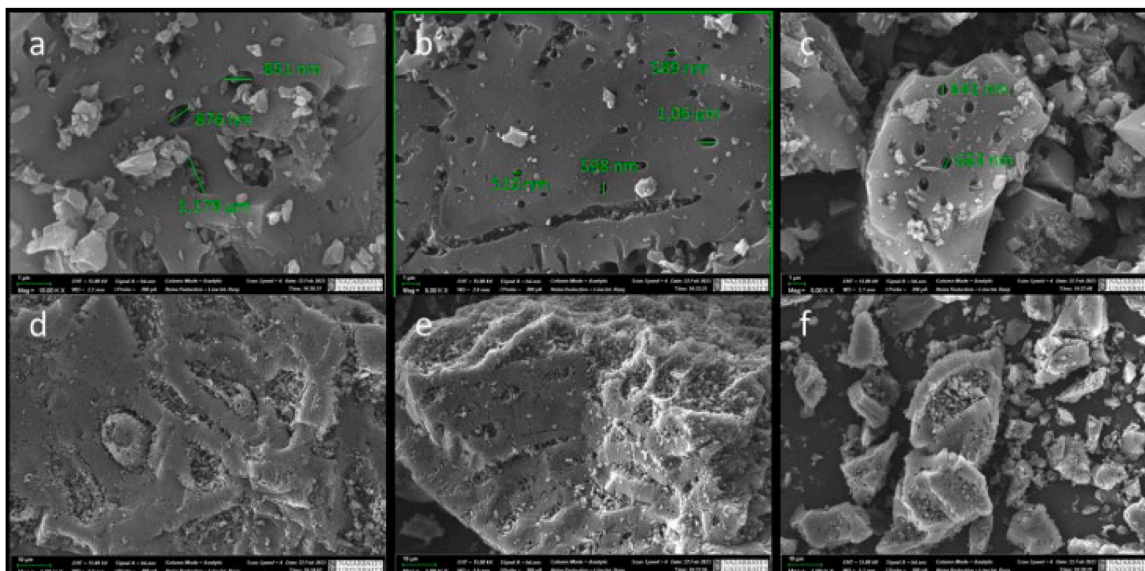


Fig 1. SEM image of cherry pit derived hard carbon without doping temperatures 1000°C (a,d), 1200°C (b,e) and 1400°C (c,f).

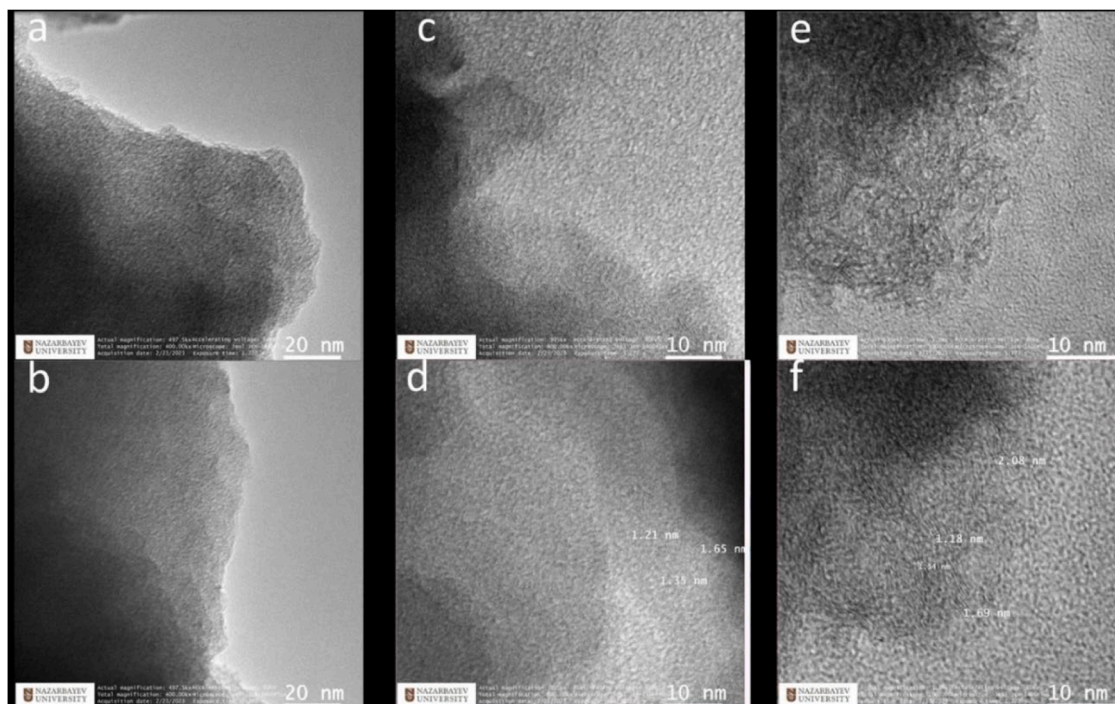


Fig 2. TEM image of bare cherry pit derived hard carbon temperatures 1000°C (a,b), 1200°C (c,d) and 1400°C (e,f).

the (002) plane, and the peak at 44° (100) plane. The slight shifting of XRD patterns to the right side was observed with temperature increment. It indicates that an increment in temperature decreases the interplanar spacing [36]. The detailed peak positions are represented in Table 1. Based on the XRD pattern the interplanar spacing between carbon sheets was identified by using the Braggs law. Where λ indicates X-ray wavelength 0.15418 nm, d corresponds to interplanar spacing. The inter-planar spacing of bare hard carbon from 0.388 nm to 0.380 nm by increasing carbonation temperature from 800°C to 1400°C. The XRD pattern of post-doping shows that no significant effect was observed on the spacing of the graphitic layer.

3.3. Raman spectroscopy analysis of hard carbon

Raman spectroscopy analysis was conducted in order to identify the graphitization degree of carbonaceous material (Figure 3b). The Wavelength of the Raman laser beam was 515 nm. Raman spectrum shows two broad peaks that approximately shift at 1330 cm^{-1} and at 1580 cm^{-1} which corresponds to D and G bands. The D band represents the disordered structure of carbon sheets and the G band represents of the presence of pseudo-graphitic domains in the material. Figure 3b illustrated Raman spectra of samples, with temperature increment there observed that the ratio of the areal intensity of G vs D bands increases, which indicates decrement of disorderness of structure and increment of graphitization degree [37]. Based on the ratio of the areal intensity of G

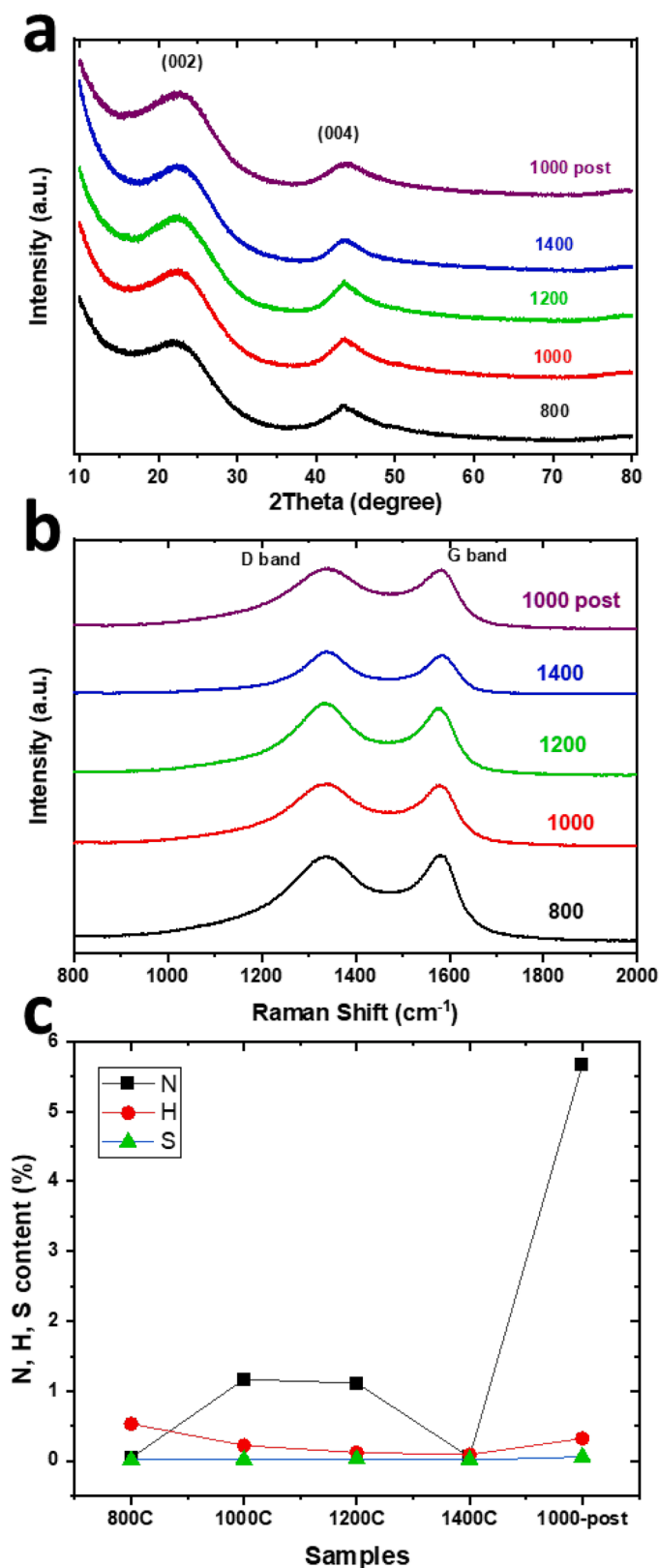


Fig 3. XRD pattern (a); Raman spectra (b); and Elemental composition (c) of the hard carbon samples.

vs D bands, doping of material affects graphitization degree, the area of the graphitic domain decreased in post-doped material. The 1000-post-doped material shows the closest result to bare material, it is due to this material was carbonized first without nitrogen dopant and creating its

Table 1

Crystallite properties of hard carbon based on XRD.

Material name	Lc (nm)	Ld (nm)	Diffraction angle 2θ
800	0.998786	0.388031	22.91835
1000	0.940727	0.385284	23.08399
1200	0.883708	0.384863	23.10958
1400	0.932586	0.380308	23.39026
1000-postdope	0.972229	0.383414	23.19815

structure and after carbonation it was undergone to post-doping. Based on Raman spectra the crystallite length in the lateral ab direction is identified according to the following equation and represented in Table 2 [38]. Based on Table 2, the lateral length of crystallites increased with increment of carbonation temperature. Urea doping suppressed of carbon layer growth in lateral direction.

3.4. CHNS Elemental analysis of hard carbon

Elemental analysis was done in order to identify the nitrogen content in hard carbon. The bare samples compared first to evaluate the nitrogen content in bare sample (Figure 3c). There identified that sample carbonized at 800°C has low nitrogen content, this could be caused by poor packing the powder into alumina foil. Based on remaining results of nitrogen, there observed that nitrogen content decreases with temperature increment, also sharp decrement observed between 1200°C – 1400°C and it could be a reason of significant differences in graphitization degree.

The hydrogen content also decreases with temperature and reaches minimum value at 1400°C. Decrement of heteroatoms from hard carbon causes the shrinking of interplanar spacing and morphology change. The doped hard carbon analysed, postdoped material carbonized at 1000°C shows high nitrogen content 5.7% (Figure 3c). There were observed interesting trend among post doped materials, the nitrogen content of post doped material is lower, especially for 1400°C. Based on this result there could be assumed that nitrogen dopant precursor reacts with hard carbon on the surface, in case of post doping, the surface of hard carbon already shrinks and less reactive for doping.

3.5. Electrochemical performance

The charge-discharge test was performed for identifying the energy capacity of the prepared electrodes. First, the effect of carbonization temperature was tested. Figure 4 illustrates the first 2 cycles of bare hard carbon charge-discharge profiles. The test was performed at a low current density of 20 mA g⁻¹, it was selected to eliminate mass transfer limitation and identify the full capacity of the material. From TEM analysis no defined graphitic domain was observed and it is correlated with the electrochemical performance of hard carbon 1000°C and 800°C, lack of graphitic domain results in small or absence of slope capacity. With an increment of carbonization temperature, there observed an increment of capacity, mainly the slope capacity. It correlates with the result of Raman spectra where with temperature the graphitization degree and lateral length of the graphitic domain are increased, and the higher lateral length of the graphitic domain provides

Table 2

Processed data from Raman spectra for La calculation.

Material name	Areal intensity of D	Areal intensity of G	I _G /I _D	L _a
800	25976.88	10386.74	0.399846	6.724268
1000	28070.11	10219.85	0.364083	6.122847
1200	23942.23	9557.2999	0.399182	6.713103
1400	20202.96	9572.817	0.473833	7.968519
1000 postdope	24602.19	8215.403	0.33393	5.615751

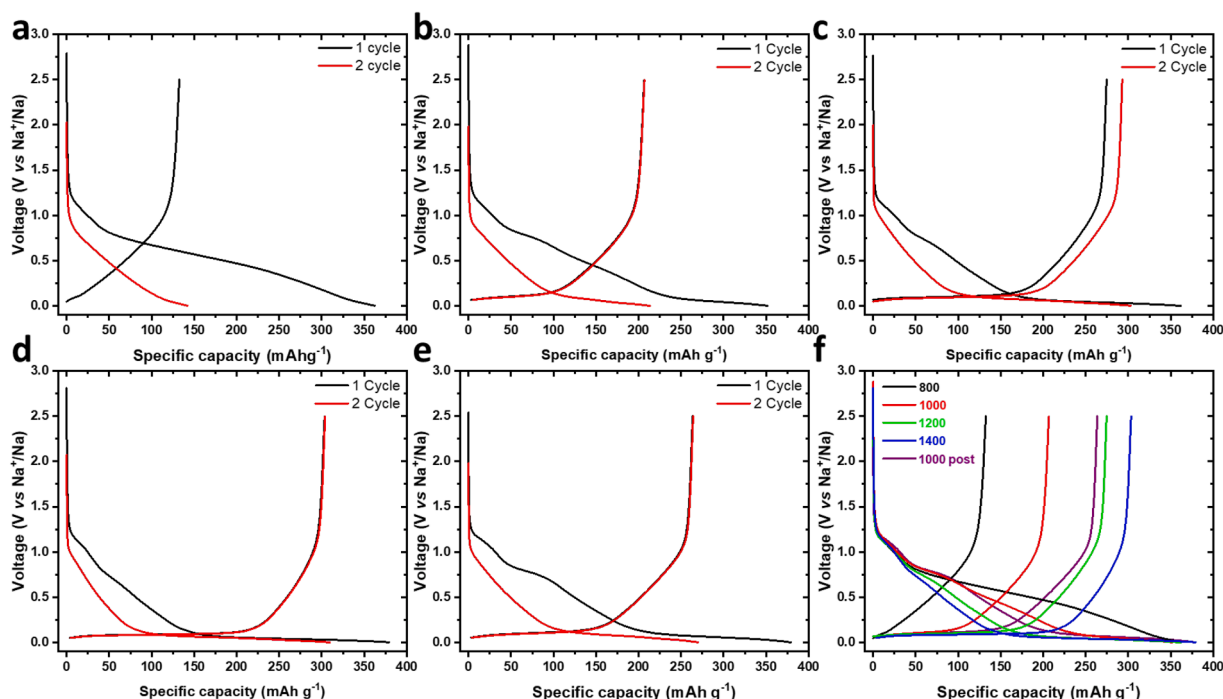


Fig 4. Voltage profiles of bare hard carbon at different temperature 800°C (a); 1000°C (b); 1200°C (c); 1400°C (d); 1000°C postdoped (e) and initial cycle comparisons (f).

a higher intercalation surface for sodium ions. Also, the initial coulombic efficiency is increasing, due to the decrement of surface area at high temperatures.

The 1000°C carbonization temperature was selected for nitrogen doping, the selection criteria were based on the knowledge that higher temperature treatment decreases the heteroatom content of the material, and the objective was to obtain higher nitrogen content in the material. Also, a slight improvement of ICE indicates a surface effect. The post-doping of the material shows further improvement in the electrochemical performance of hard carbon (Figure 4, Table 3). The high capacity of post-doping is the result of moderate graphitization, high interplanar spacing, and surface doping with nitrogen. Moreover, electrochemical impedance spectroscopy (EIS) results in Figure 5a reveal that the post-doped sample demonstrates a reduced charge transfer resistance relative to the undoped sample, indicating improved electronic conductivity and enhanced interfacial charge transport kinetics.

The hard carbon material prepared at temperatures 1400°C showed highest results in low current rate, however it only provides information about maximum capacity of electrode. In order to obtain complete electrochemical performance of materials batteries tested at 5 different current rates 20 mA g⁻¹, 50 mA g⁻¹, 100 mA g⁻¹, 500 mA g⁻¹ and 1000 mA g⁻¹ (Figure 5b). The hard carbon derived at 1500°C has the highest capacity 305 mAh g⁻¹ at 50 mA g⁻¹ current rate, at 100 mA g⁻¹ the capacity decreased to 244 mAh g⁻¹. This decrement is the result of concentration polarization on the surface of electrodes. The transition moment from 100 mA g⁻¹ to 500 mA g⁻¹ shows a significant drop in capacity of hard carbons derived 1400°C and 1500°C. Unfortunately, batteries with hard

carbon 1200°C shorted. The huge capacity decrement at 500 mA g⁻¹ is probably result of mass transfer limitation, due to insufficient time for adsorption of sodium into inner part of hard carbon and for intercalation reaction. It means that at high current rate adsorption proceeds only on the easily assessable surface of hard carbon. At 1 A g⁻¹ capacity drop to 53 mAh g⁻¹. All bare electrodes show similar behavior and capacity at 1 A g⁻¹, however nitrogen post doped hard carbon shows good capacity retention 110 mAh g⁻¹ at 1 A g⁻¹. Probably the reason for such improvement of electrochemical performance at high current rate is nitrogen doping enhanced surface of material.

To gain deeper insight, the diffusion behavior of Na⁺ ions was studied. Using GITT and Fick's law, the diffusion coefficient (log(D_{Na})) was determined. As shown in Figure 5c and 5d, during both discharge and charge processes, the diffusion coefficient consistently declined. These phenomena was well matched with reference previously published [30].

The cycling performance at a current density of 20 mA g⁻¹, as shown in Figure 5e, demonstrates stable behavior, retaining nearly 100% of its capacity from the 2nd cycle even after 50 cycles. In order to evaluate performance, it is required to compare with results of other work (Table 4). Mangosteen derived hard carbon provided capacity 180 and 330 mAh g⁻¹ at temperatures 1000°C and 1500°C, respectively. In this work at 1000°C with nitrogen doping 263 mAh g⁻¹ obtained, and bare material at 1500°C provided 319 mAh g⁻¹ [39]. From wood Shen et.al. obtained 260 mAh g⁻¹ capacity, the method that was used is oxidation by adding oxidation reagent [40]. Pomelo peel derived hard carbon shows impressive capacity, activation with phosphoric acid strategy was used

Table 3
Summary on electrochemical performance of cherry pit derived hard carbon.

Material	Irreversible capacity (mAh g ⁻¹)	Reversible capacity (mAh g ⁻¹)	ICE (%)	Plateau capacity 0V -0.1V (mAh g ⁻¹)	Slope capacity 0.1V-2.5V (mAh g ⁻¹)
800	362.29	132.48	36.57	36.58	95.90
1000	351.59	206.64	58.77	111.18	95.47
1200	361.65	274.57	75.92	186.02	88.54
1400	382.22	304.84	79.75	215.42	89.42
1000-postdope	379.24	263.60	69.51	143.13	120.47

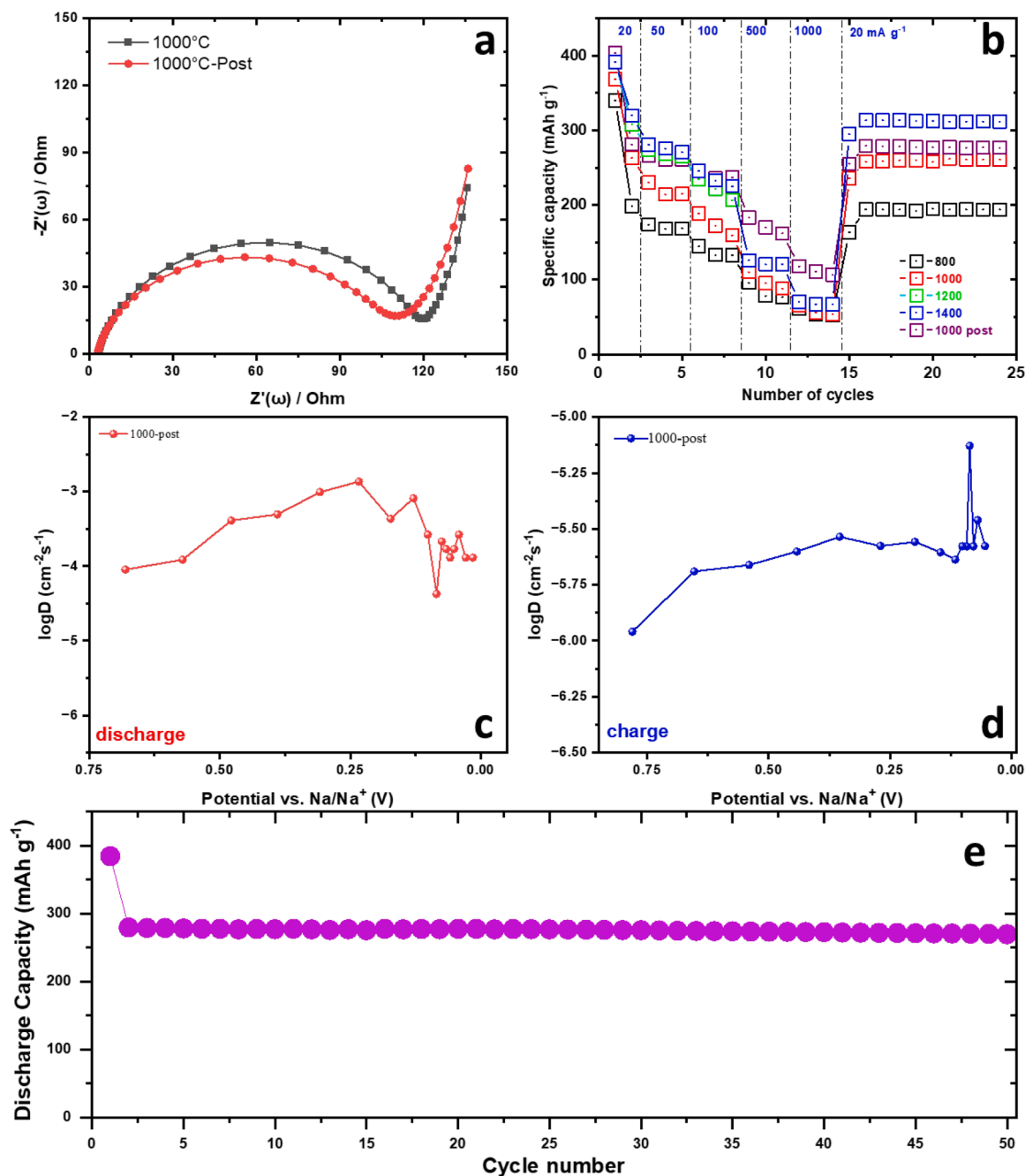


Fig 5. Electrochemical performance of hard carbons (a) EIS impedance, (b) at different current rate, (c,d) GITT analysis and (e) cycleability at 20 mA g^{-1} .

to obtain such performance [41]. Cotton derived hard carbon at 1300°C by Li et.al. illustrates good capacity at current rate 30 mA g^{-1} , however at lower temperatures the significant decrement of specific capacity was observed [42]. Best electrochemical performance of cellulose derived hard carbon observed at carbonization temperature range of 1400-1600°C.

4. Conclusion

In summary, hard carbon was successfully synthesized using a simple pyrolysis method for sodium-ion batteries (SIBs), with a detailed analysis of temperature effects. Various nitrogen doping strategies were employed to enhance its electrochemical performance, characterized by techniques such as SEM, TEM, XRD, Raman spectroscopy, and CHNS analysis. The results showed that nitrogen doping suppresses the growth

of graphitic crystallites in hard carbon, reducing available intercalation sites for sodium ions. However, these crystallites remain important for intercalation efficiency. Galvanostatic charge-discharge analysis indicated that carbonization at 1500°C yields the highest capacity. While higher temperatures increase graphitic domain size and plateau capacity, they also decrease slope capacity due to limitations in adsorption-desorption processes. Nitrogen post-doping proved to be the most effective method, enhancing the capacity of hard carbon treated at 1000°C from 206 mAh g^{-1} to 236 mAh g^{-1} . Although nitrogen doping slightly improved the initial coulombic efficiency (ICE) at this temperature, optimal ICE requires higher temperatures, which reduce heteroatom content. Further studies are needed to evaluate the performance of the synthesized material at higher current rates. Cycling tests at various current rates demonstrated that nitrogen post-doping enhances capacity at elevated currents. Overall, this work highlights nitrogen doping as a

Table 4

Electrochemical performance comparison with other works.

Material	Temperature (°C)	Reversible capacity (mAh g ⁻¹)	Current rate (mA g ⁻¹)	ICE (%)	Ref.
Mangosteen	1000	180	20	55	[39]
Mangosteen	1500	330	20	83	[39]
Wood	1000	260	20	72	[40]
Pomelo peels	700	236	200	27	[41]
Hollow carbon nanofiber	700	174	50	41	[43]
N-doped porous hollow carbon nanofibers	700	190	50	32	[43]
Cotton	1300	315	30	83	[42]
Cotton	1000	88	30	26	[42]
Cellulose	1600	310	37	83	[44]
Cherry pit N doped	1000	259	50	69	This work

promising approach to optimize hard carbon for sodium-ion battery applications.

CRedit authorship contribution statement

Maksat Maratov: Writing – original draft, Methodology, Investigation, Data curation, Conceptualization. **Aibar Alpysbayev:** Methodology, Investigation, Data curation. **Dilshat Abduakhitov:** Methodology, Investigation, Data curation. **Bauyrzhan Myrzakhetov:** Data curation, Formal analysis, Visualization. **Kenes Kudaibergenov:** Visualization, Validation, Formal analysis. **Zhumabay Bakenov:** Visualization, Validation, Formal analysis. **Seung-Taek Myung:** Visualization, Validation, Formal analysis, Conceptualization. **Aishuak Konarov:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition.

Declaration of competing interest

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

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Data availability

Data will be made available on request.

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