

**Sucrose-Impregnated Biowaste Hard Carbon Synthesized
Through Co-Carbon Strategy for Advanced Sodium-Ion Battery
Applications**

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Declaration

This thesis, entitled "Sucrose-Impregnated Biowaste Hard Carbon Synthesized Through Co-Carbon Strategy for Advanced Sodium-Ion Battery Applications," represents my original research effort. Where the work of others has been referenced, appropriate attribution has been provided. I further confirm that no part of this document has been previously or concurrently presented in pursuit of any other academic award at Nazarbayev University or elsewhere.



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Abstract

Hard carbon obtained from walnut shells has attracted considerable attention as a low-cost and environmentally sustainable anode material for sodium-ion batteries. One persistent challenge, however, is the insufficient presence of closed micropores — small sealed voids within the carbon structure that are essential for trapping sodium ions and achieving high initial coulombic efficiency (ICE). When these closed pores are lacking, a significant fraction of sodium is consumed irreversibly during the first cycle, lowering overall cell efficiency. To overcome this limitation, the present study employed a sucrose impregnation approach in which pre-carbonized walnut shell hard carbon was soaked in sucrose solutions of different concentrations and then heat-treated under an inert atmosphere. During pyrolysis, the sucrose decomposed into a thin soft carbon layer that coated the particle surface, sealed open pores, and introduced new closed porosity. The resulting material exhibited a composite co-carbon architecture — a rigid, disordered hard carbon core wrapped in a conformal soft carbon shell — which improved ion transport and increased the number of active sodium storage sites.

A range of characterization techniques confirmed these structural and chemical changes. XRD and Raman spectroscopy showed that sucrose treatment widened the interlayer spacing and reduced defect density while maintaining the overall turbostratic carbon framework. SEM and TEM images revealed that the particle surfaces became progressively smoother with increasing sucrose concentration, and EDS mapping indicated a uniform distribution of oxygen throughout the samples. XPS analysis further demonstrated a reduction in surface oxygen-containing functional groups after coating, which is beneficial for forming a stable solid electrolyte interphase (SEI) and minimizing side reactions during cycling.

Electrochemical testing highlighted the critical role of sucrose concentration. Among all samples, the 0.25 M treatment delivered the best overall performance, reaching an ICE of roughly 80% with reliable capacity retention over extended cycling and across varying current densities. Higher concentrations of 0.5 and 1 M still showed improvements over bare hard carbon, but the thicker carbon layer and elevated oxygen content gradually compromised electronic conductivity and long-term stability. These findings show that sucrose impregnation is a simple, scalable, and cost-effective method for enhancing the performance of biomass-derived hard carbon anodes in sodium-ion batteries, offering a practical route toward affordable and efficient energy storage.

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List of Abbreviations and Symbols

HC	Hard carbon
SC	Soft carbon
HC-WS	Hard carbon derived from walnut shells
HC-S	Hard carbon coated with sucrose
SIB	Sodium-ion batteries
LIB	Lithium-ion batteries
ICE	Initial coulombic efficiency
SEI	solid electrolyte interphase
XRD	X-ray diffraction
SEM	Scanning electron microscope
TEM	Transmission electron microscope
EDS	Energy-dispersive X-ray spectroscopy
XPS	X-ray photoelectron spectroscopy
PVDF	polyvinylidene fluoride
NMP	N-methyl-2-pyrrolidone
AB	Acetylene black
EC	ethylene carbonate
DEC	diethyl carbonate

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Chapter 1 Introduction

1.1 Global energy demand and environmental issues

The growing global population and widespread adoption of modern technology have generated an unprecedented demand for electricity [1]. Between 1990 and 2020, the world's population increased from approximately 5 billion to over 8 billion, and global electricity consumption more than doubled during the same period [2]. Electricity powers homes, industry, and information technology, but most electricity is currently generated by burning coal, oil, and natural gas. Burning fossil fuels releases large quantities of carbon dioxide and other greenhouse gases, which trap heat in the atmosphere and exacerbate climate change [3]. Measures to mitigate global warming, such as the 2015 Paris Agreement, require significant reductions -in greenhouse gas emissions and a rapid transition to renewable energy sources. [4][5]. Solar and wind power have developed rapidly in recent years. Wind and solar power cover approximately 82% of the growing electricity demand and provide 30% of the world's electricity supply from renewable energy sources [6]. However, renewable energy is intermittent, as its production depends on weather and sunlight, so without some form of energy storage, it is impossible to supply electricity on demand.

1.2 The need for highly efficient energy storage systems

Energy storage devices bridge the gap between intermittent renewable energy generation and continuous electricity demand. Mature energy storage technologies, such as pumped-storage hydroelectric plants, compressed air storage systems, and flywheel energy storage systems, allow for the storage of large amounts of energy. However, they also have significant drawbacks: they can only be used in locations that meet specific topographical or geological conditions. Other energy storage technologies often lack sufficient power density, limiting their use in many applications [7][8][9]. Electrochemical batteries offer a very attractive alternative. They can be installed virtually anywhere and offer high efficiency throughout the charge and discharge cycle. A battery consists of four key components: a cathode (positive electrode), an anode (negative electrode), a separator (which prevents direct contact between the two electrodes), and an electrolyte (which serves as the medium for transporting ions between the two electrodes) [10][11]. During discharge, electrons flow from the anode to the cathode through the external circuit, while ions move within the electrolyte to maintain charge balance; during charging, the process is reversed. The battery voltage depends on the electrochemical potential difference between the electrodes.

Lithium-ion batteries (LIBs) currently dominate the portable electronics and electric vehicle markets, as lithium is the lightest metal and has a very low standard reduction potential (-3.01 V with respect to a standard hydrogen electrode) [9][10]. These properties allow LIBs to achieve high energy density and long lifespans [11]. A typical LIB -uses transition metal oxides or phosphates as the positive electrode, graphite as the negative electrode, and organic carbonates as the electrolyte [12]. However, the rapid growth of electric vehicles and stationary energy storage systems has put pressure on the lithium supply chain. The price of lithium quadrupled between 2007 and 2017, and demand for lithium, nickel, and graphite is projected to increase 14 to 20 times by 2020 and even more by 2040 [9]. Lithium resources are geographically concentrated in a few countries, and their extraction requires significant water resources, raising social and environmental concerns. These factors increase costs, driving the search for batteries based on more abundant elements.

1.3 Sodium-ion batteries as an alternative

Sodium-ion batteries (SIBs) have emerged as a promising alternative to lithium-ion batteries (LIBs) for large-scale energy storage. Sodium is [13][14] the sixth-most abundant element in Earth's crust and can be extracted inexpensively from seawater and salt deposits [15]. Like lithium, sodium forms monovalent ions and belongs to the alkali-metal group. However, sodium atoms are heavier than lithium atoms (atomic mass of 23 g mol^{-1}) and have a larger ionic radius ($1.02 \text{ \AA}$), while lithium atoms have an atomic mass of 6.9 g mol^{-1} and an ionic radius of $0.76 \text{ \AA}$; furthermore, the standard reduction potential of sodium is slightly less negative (-2.71 V) [16][17]. These characteristics result in sodium-ion batteries (SIBs) having lower voltage and energy density per cell than lithium-ion batteries. Nevertheless, they also offer advantages. For example, sodium-ion batteries can employ aluminum as the negative electrode current collector instead of the more expensive copper. More importantly, sodium is globally abundant and substantially cheaper than lithium, making sodium-ion batteries ideal for large-scale stationary energy storage systems, where cost reduction is more important than achieving maximum volumetric energy density. Sodium-ion batteries (SIBs) and lithium-ion batteries (LIBs) operate on analogous electrochemical principles [13][16]. During charging, sodium ions deintercalate from the positive electrode (cathode) and migrate toward the negative electrode (anode); during discharge, the process is reversed, as shown in Figure 1. One of the main challenges of sodium-ion batteries is the relatively large ionic radius of Na^+ , which impedes its incorporation into conventional anode materials. For example, graphite has an interlayer spacing of approximately 0.335 nm [18]. While graphite readily intercalates

lithium to form LiC_6 with a theoretical capacity of 372 mAh g^{-1} , it can only form thermodynamically unstable compounds with sodium at ambient temperature [16][19]. Consequently, the identification of suitable alternative anode materials remains imperative for sodium-ion battery development.

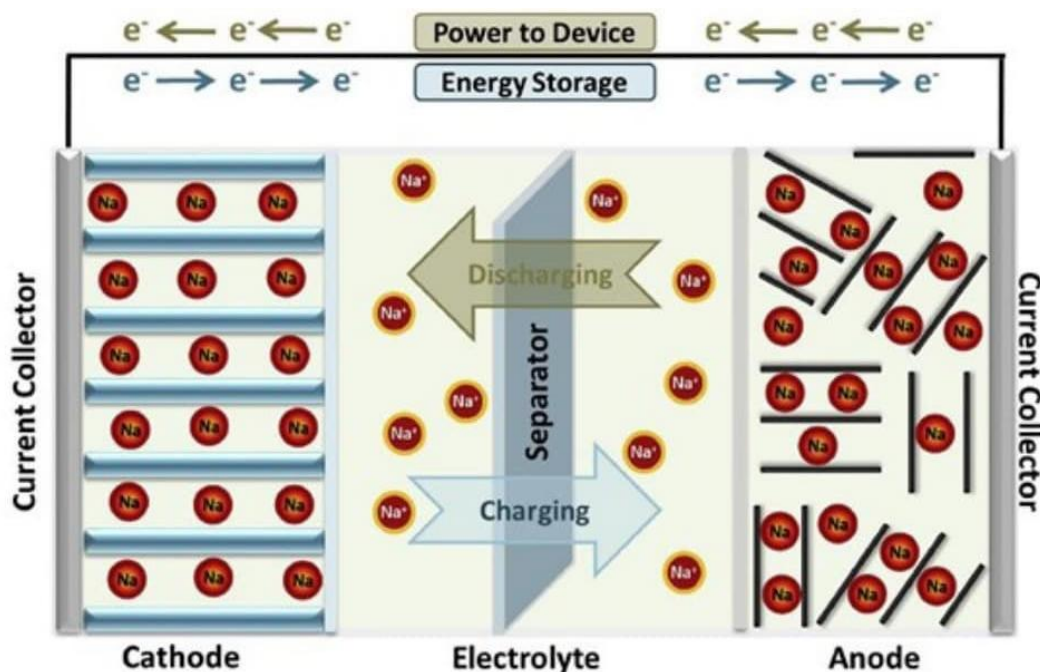


Figure 1. Working principle of a sodium-ion battery [20]

1.4 Comparison of the characteristics of lithium and sodium batteries

Since lithium and sodium belong to the same group in the periodic table, comparing their fundamental properties helps elucidate the relationship between the lower energy density and potential cost advantages of sodium-ion batteries (SIBs) [21]. Table 1 summarizes the key physical and electrochemical parameters [22]. Compared to lithium, sodium has a larger ionic radius, a higher atomic mass, and a marginally lower electronegativity. Furthermore, its standard reduction potential is less negative, resulting in a cell voltage approximately 0.3 V lower than that of lithium-ion batteries (LIBs). However, sodium is vastly more abundant in the Earth's crust than lithium (23,600 ppm compared to only 20 ppm for lithium), and it is considerably less expensive per tonne. These substantial differences are important for selecting suitable anode materials and for overall battery design [8].

Table 1. Properties of sodium and lithium [22]

Property	Lithium	Sodium
Atomic mass (g mol^{-1})	6.94	22.99

Ionic radius (Å)	0.76	1.02
Standard reduction potential (V vs SHE)	-3.01	-2.71
Electronegativity (Pauling)	0.98	0.93
Abundance in Earth's crust (ppm)	20	23,600
Approximate price (USD t ⁻¹)	~10,000	~150

1.5 The role of anode materials and hard carbon

For sodium-ion batteries (SIBs), the development of suitable anode materials remains the most formidable challenge [23][24]. Carbon-based materials represent promising candidates for this role owing to their low cost, robust chemical stability, and moderate voltage plateau. It is well established that graphite cannot reversibly intercalate sodium ions under standard conditions. This is because sodium ions (Na⁺) have a large ionic radius, and their unfavorable intercalation thermodynamics preclude the formation of stable graphite intercalation compounds, in contrast to lithium ions [12][25]. Hard carbon (HC) and soft carbon (SC) are non-graphitic carbon materials derived from the pyrolysis of organic precursors at temperatures typically ranging from 900 to 1500 °C [22][26]. Structurally, they consist of turbostratically arranged graphene sheets with irregular interlayer spacing, high nanopore density, and random crystallite orientation [22]. The fundamental distinction between these two materials resides in their internal microstructure: HC possesses a highly disordered framework with predominantly closed porosity, whereas SC retains a degree of long-range structural order and typically exhibits a higher specific surface area. The expanded interlayer spacing and nanoscale porosity of HC furnish favorable accommodation sites for Na⁺ ions, establishing it as one of the most promising anode materials for sodium-ion batteries. This material can provide a reversible capacity in the range of 250-350 mAh g⁻¹ with an initial coulombic efficiency (ICE) exceeding 80% [8][27][28]. However, hard carbon is not without its limitations. A principal drawback is the considerable irreversible capacity loss observed during the initial charge-discharge cycle [29]. A fraction of sodium ions becomes irreversibly trapped within structural defects and micropores, while an additional portion is consumed during the formation of the solid electrolyte interphase (SEI). The resultant diminution in ICE reduces the overall specific energy of the cell, necessitating the incorporation of excess anode material as compensation. Various mitigation strategies have been investigated, including tailoring precursor composition, controlling pore size and distribution through acid washing and pre-oxidation treatments, and applying surface coatings to stabilize the SEI layer [30]. The present study

examines one such approach: the utilization of sucrose as a coating agent to modify the surface of hard carbon derived from walnut shells.

1.6 Scope and objectives of this thesis

Using solid carbon derived from walnut shells as the negative electrode material. Walnut shells are a common agricultural residue rich in lignin and cellulose, which can be pyrolyzed to produce carbon materials with a hierarchical porous structure. Previous studies on walnut shell carbon showed that its reversible capacity is approximately 257 mAh g^{-1} , and it maintains good cyclic stability after 300 cycles [6]. However, its initial coulombic efficiency (ICE) is still low (around 70%) due to surface defects and micropore trapping. To address this problem, in this study, the surface of the walnut shell-derived solid carbon was coated with a sucrose-derived carbon film. Sucrose is an inexpensive and abundant disaccharide that can be broken down by heating to produce carbon-containing materials. This study hypothesizes that the sucrose coating can smooth the surface of solid carbon, reduce the accessible surface area, and thus improve the initial coulombic efficiency without blocking the sodium ion storage sites.

Specific objectives:

1. **Production of sucrose-coated hard carbon anodes.** First, walnut shells are acid-treated, cleaned, and pre-carbonized to produce hard carbon; then, the walnut shells are coated with sucrose of different concentrations (e.g., 0.25 M, 0.5 M, and 1.0 M) to form a soft carbon layer.
2. **The microstructure and surface properties of the anode were studied.** The effect of the sucrose coating on the interlamellar spacing, defect density, and pore structure of the solid carbon anode was characterized by X-ray diffraction, Raman spectroscopy, BET surface area analysis, and electron microscopy.
3. **The electrochemical properties of sodium-ion batteries were evaluated.** Sodium-ion battery half-cells with and without sucrose-coated anodes were fabricated and studied to investigate their initial coulombic efficiency, capacity retention, and rate characteristics. A relationship between sucrose concentration and final electrochemical behavior, along with observed structural changes, was established.

Chapter 2. Literature Review

2.1 Overview of sodium-ion batteries

Sodium-ion batteries (SIBs) consist of the following components: a positive electrode ($\text{Na}_3\text{V}_2(\text{PO}_4)_3$), a sodium-ion conducting electrolyte (e.g., sodium hexafluorophosphate dissolved in a carbonate solvent), a separator, and a negative electrode. During electrochemical operation, Na^+ ions move reversibly between the positive and negative electrodes, while electrons are transported through an external circuit. Compared to Li^+ , Na^+ has a larger ionic radius and a lower negative electrochemical potential, resulting in a lower average operating voltage and specific energy than lithium-ion batteries (LIBs). However, the abundant natural reserves and low cost of sodium offset these disadvantages. A prototype sodium-ion battery using a positive electrode of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ and a negative electrode of hard carbon demonstrated a specific energy of approximately 160 Wh kg^{-1} , comparable to that of early lithium-ion batteries and sufficient for stationary energy storage systems.

Table 1 compares the properties of lithium and sodium. Figure 2 shows typical structures of graphite, soft carbon, and hard carbon [22]. Graphite consists of stacked graphene layers with an interlayer spacing of 0.335 nm , demonstrating long-range order. Soft carbon retains some graphitic domains, but its stacking is disordered, resulting in numerous defects. Hard carbon is highly disordered, consists of randomly oriented curved graphene sheets, and contains numerous nanopores. The presence of nanopores and a large interlayer spacing ($>0.36 \text{ nm}$) in hard carbon allows for the insertion and adsorption of Na^+ ions.

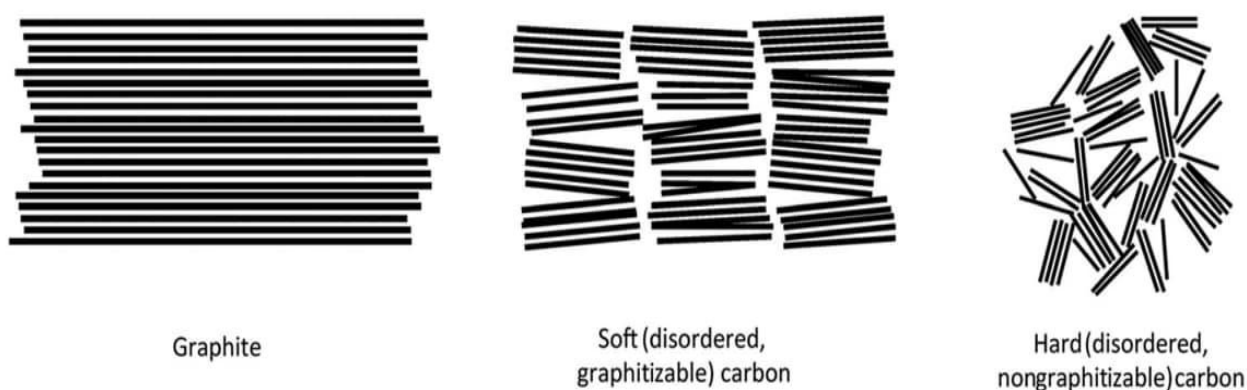


Figure 2. Graphite structure along with soft carbon and hard carbon.[22]

2.2 Anode materials for sodium-ion batteries

Sodium-ion battery anode materials can be divided into three main categories, based on the reaction mechanism [31]:

1. **Conversion anodes.** Metal oxides (e.g., Fe_2O_3), sulfides (e.g., FeS_2), phosphides, and nitrides react with sodium to form Na_2X and metal nanoparticles. These reactions can provide high capacities ($>400 \text{ mAh g}^{-1}$), but involve the complete breaking and recombination of chemical bonds, leading to significant volume changes and voltage hysteresis. Therefore, cycle stability is often compromised due to the decay of the active material and the resulting loss of electrical contact.
2. **Alloy anodes.** Elements such as tin, antimony, phosphorus, and bismuth form intermetallic alloys with sodium (e.g., $\text{Na}_{15}\text{Sn}_4$), which exhibit extremely high theoretical capacities ($>500 \text{ mAh g}^{-1}$). However, alloy formation is accompanied by significant volume expansion; for example, $\text{Na}_{15}\text{Sn}_4$ expands by approximately 420% compared to Sn, resulting in reduced mechanical properties and accelerated capacity decline. Nanostructuring and matrix damping strategies have been proposed to mitigate these effects, but these entail increased fabrication complexity and cost [20].
3. **Intercalation and adsorption anode materials.** Carbon materials and titanium-based oxides accumulate Na^+ ions through a combination of intercalation between graphene layers and adsorption within the porous structure. Among these, hard carbon has become the most practical anode material for sodium-ion batteries due to its moderate specific capacity, low average operating potential (0.1-0.2 V vs. Na^+/Na), and satisfactory cyclic stability. Its main drawbacks include a relatively low initial coulombic efficiency and significant hysteresis between the charge and discharge curves [18].

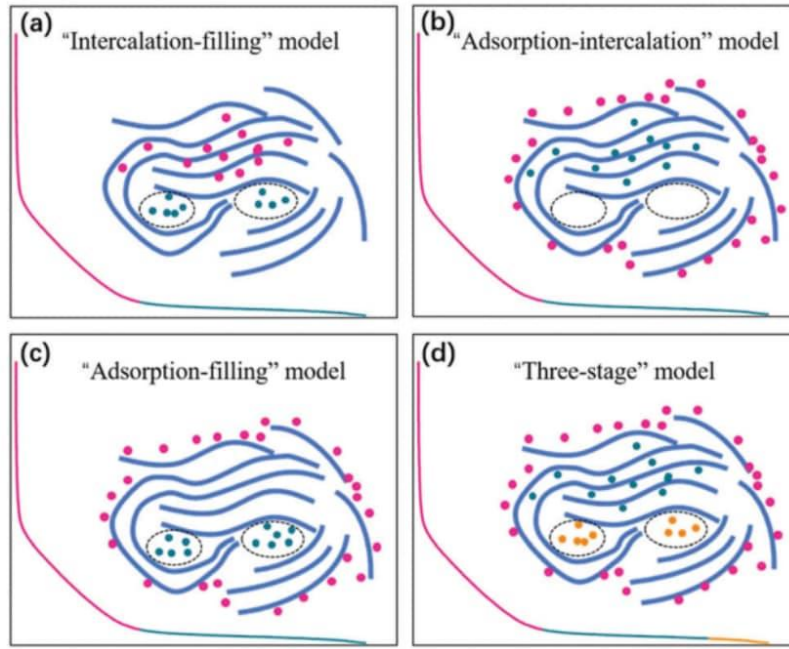


Figure 3. Uptake of sodium and its mechanism in hard carbon [22]

2.3 Mechanism of sodium storage in solid carbon

Understanding how sodium is stored in hard carbon is crucial for optimizing its electrochemical performance. Stevens and Dan initially proposed a two-band model, where the sloping region (above approximately 0.1 V) corresponds to Na^+ intercalation between graphene layers, while the low-voltage plateau region is explained by pore filling or surface adsorption [8][32]. Subsequent studies revealed more complex storage processes. Cao et al. proposed an improved three-stage mechanism that describes the discharge curve from several perspectives: (i) Na^+ adsorption at defect sites and functional groups in the sloping region; (ii) Faraday reactions on microporous surfaces in the initial plateau region; and (iii) quasimetallic filling of nanopores with sodium at low voltage [29]. Further studies highlighted the role of nanopores and surface defects in trapping Na^+ ions, leading to irreversible capacity loss. Therefore, controlling pore size distribution, increasing interlayer spacing, and minimizing specific surface area are considered key strategies for improving the initial coulombic efficiency and rate performance of hard carbon anodes.

2.4 Hard carbon derived from biomass

Biomass represents a highly promising precursor for hard carbon synthesis owing to its widespread availability, renewable nature, and low cost [19][22]. The composition of the biomass feedstock, particularly the relative proportions of cellulose, hemicellulose, and lignin, directly governs the yield and microstructure of the resultant carbon material. Cellulose and

hemicellulose undergo thermal decomposition at relatively low temperatures (approximately 200-400 °C), generating volatile byproducts, whereas lignin degrades over a broader temperature range (200-500 °C), yielding aromatic carbon residues [33]. The relative abundance of these constituents determines the porosity and degree of graphitization of the derived carbon. Table 2 summarizes the electrochemical properties of various hard carbon materials obtained from biomass precursors. Acid washing and pre-oxidation constitute common pretreatment methods for removing inorganic impurities and refining pore architecture. Hard carbon derived from microcrystalline cellulose exhibits a reversible capacity of approximately 340 mAh g⁻¹ and an initial coulombic efficiency (ICE) of 69%, benefiting from its high cellulose content and the removal of ash constituents through acid washing. Lignin-derived hard carbon demonstrates a higher degree of irreversible sodium-ion trapping, resulting in a comparatively lower ICE of approximately 60%. Apple pomace-derived hard carbon yielded a reversible capacity of 285 mAh g⁻¹ with an ICE of 65.6%, attributed to its high closed-pore volume and low BET surface area. Lotus stem-derived carbon, following carbonization at 1400 °C, delivered a capacity of 351 mAh g⁻¹ with an ICE of 70%, facilitated by its microtubular channel structure that promotes Na⁺ diffusion. Triodia grass, after carbonization at 1000 °C, exhibited a capacity of 386 mAh g⁻¹; however, its ICE diminished considerably to 50%, a consequence of delignification enhancing cellulose content at the expense of increased surface reactivity. Walnut shell-derived hard carbon, pyrolyzed at 800-1200 °C, achieved a reversible capacity in the range of 257-362 mAh g⁻¹ with an ICE of approximately 70%, benefiting from its abundant waste availability and a pyrolysis process that yields hierarchical porosity. These superior electrochemical performances are attributed to the prevalence of closed-pore structures, which enhance the plateau capacity contribution.

Table 2. Precursors' performance for SIBs where hard carbon derived from biomass

Biomass precursor	Carbonization temperature (°C)	Reversible capacity (mAh g⁻¹)	ICE (%)	Notes
Microcrystalline cellulose	900	≈340	69	High cellulose content; acid washing reduces ash [34]
Lignin	1300	≈230	60	Larger amount of trapped Na; lower ICE [18]
Apple pomace	1100	285	65.6	High closed pore volume, low BET surface area [35]

Lotus stem	1400	351	70	Microtubular channels facilitate Na diffusion [27]
Triodia grass	1000	386	50	Delignification increases cellulose content [24]
Walnut shell	800-1200	257-362	~70	Abundant waste; pyrolysis yields hierarchical pores [36]

Taken together, these results demonstrate that both biomass composition and processing conditions significantly affect the electrochemical performance of solid carbon. Precursors with high cellulose and hemicellulose content typically provide higher initial coulombic efficiency (ICE), as the lower number of active sites on the surface limits irreversible sodium ion adsorption. Acid washing removes inorganic salts that would otherwise promote undesirable side reactions and hinder the formation of a porous structure. Pre-oxidation introduces oxygen-containing surface functional groups, which promotes sodium ion adsorption ; however, this process must be strictly controlled to avoid excessive increases in specific surface area. Chemical activation using reagents such as potassium hydroxide (KOH) or zinc chloride (ZnCl_2) can create micropores and mesopores, thereby increasing specific capacity, but generally results in a decrease in initial coulombic efficiency due to the increased surface area and greater formation of the solid electrolyte interphase (SEI). Therefore, the rational selection of precursor materials and the optimization of processing conditions are crucial for producing hard carbon anodes with balanced performance.

2.5. The walnut shell as a precursor of solid carbon.

Walnut shells are a promising biomass feedstock for the synthesis of solid carbon materials, as they are a byproduct of food production and possess a balanced composition of lignin, cellulose, and hemicellulose. Yan et al. synthesized solid carbon materials using charred walnut shells, followed by hydrothermal treatment with hexadecyltrimethylammonium bromide (CTAB) and potassium hydroxide (KOH) [37]. Scanning electron microscopy revealed a dense granular morphology characterized by micropores that facilitate electrolyte diffusion; high-resolution transmission electron microscopy revealed that the hydrothermal treatment converted some micropores into mesopores, thereby improving the diffusion kinetics of sodium ions (Na^+). The CTAB/KOH treated sample (CWS-CK) exhibited a reversible capacity of 283.7 mAh g^{-1} at a current density of 0.02 A g^{-1} , which was approximately 83% higher than that of

the untreated hard carbon, and retained a capacity of 189.4 Ah after 320 cycles at a current density of 0.2 A g^{-1} .

In previous studies on carbon materials derived from walnut shells, we explored a relatively simple synthesis method: walnut shells were washed, dried, and then pyrolyzed at 800-1200 °C under an inert atmosphere [36]. The resulting solid carbon exhibited a reversible capacity of 257 mAh g^{-1} at a current density of 50 mA g^{-1} and showed good cycling stability after 300 cycles. Acid washing prior to carbonization effectively removed inorganic impurities and improved the material's surface properties. However, due to the presence of numerous micropores and surface defects, its initial coulombic efficiency (ICE) remained low, at approximately 70%. Overall, these studies highlight the significant potential of walnut shells as a precursor to solid carbon and point to the need for surface modification strategies to improve the initial coulombic efficiency.

2.6 Soft carbon and sucrose-derived coatings

The difference between soft carbon and hard carbon lies in the fact that soft carbon retains some of the ordered structural domains of graphite, while also possessing greater interlayer spacing and a larger specific surface area. It is typically produced by the pyrolysis of resin, glucose, sucrose, or synthetic polymers at temperatures ranging from 800 to 1200 °C. Research has shown that coating hard carbon with soft carbon can improve initial coulombic efficiency (ICE) by passivating rough surfaces, covering structural defects, and reducing the surface area available for electrochemical processes. For example, researchers have coated hard carbon with resin or polymer resins to form a thin, low-porosity coating, which limits the formation of a solid electrolyte interfacial (SEI) layer. In recent years, sucrose-derived carbon materials have attracted attention due to their low cost, renewable nature, and ability to decompose into carbonaceous materials at moderate temperatures. A study of sucrose-derived carbon (SC900) demonstrated a discharge capacity exceeding 100 mAh g^{-1} after 400 cycles, with improved structural ordering that increases both capacity and stability [23]. When used as a coating for other carbon materials, sucrose improves the initial coulombic efficiency (ICE) and rate performance by forming a more uniform SEI film. Sucrose is composed of glucose and fructose units and has a melting point of approximately 185 °C. When heated in an inert atmosphere, it initially dehydrates, forming a carbonaceous solid and releasing water and carbon monoxide. At higher temperatures, the material becomes more graphitized. Methods for coating hard carbon (HC) with sucrose involve immersing the carbon powder in a sucrose solution and then carbonizing it after drying. The resulting soft carbon layer is expected to seal accessible

micropores and reduce the overall defect density, while maintaining sufficient porosity for unimpeded diffusion of Na^+ ions. To date, relatively little research has been conducted on the application of sucrose-based coatings to hard carbon derived from walnut shells; therefore, this study aims to fill this gap in the existing literature.

2.7 Summary and gaps in the research

A literature review shows that sodium-ion batteries are a viable and increasingly competitive alternative to lithium-ion batteries, particularly well-suited for stationary energy storage systems. Solid carbon remains the most practical anode material for sodium-ion batteries; its structural characteristics, larger layer spacing, and easily accessible nanopores allow for the efficient incorporation of relatively large Na^+ ions through intercalation and pore-filling mechanisms. Solid carbon derived from biomass offers significant advantages in terms of environmental friendliness and production cost; some precursors, such as bagasse and apple pomace, have demonstrated high initial coulombic efficiency and satisfactory reversible capacity. Solid carbon derived from walnut shells has a hierarchical porous structure and competitive capacity; however, its initial coulombic efficiency remains relatively low. Surface modification methods, including acid washing, pre-oxidation, and heteroatom doping, have been shown to improve electrochemical performance, but heteroatom doping significantly alters the chemical structure of the carbon framework, which is beyond the scope of this study.

Soft carbon coatings, particularly those prepared by sucrose pyrolysis, have shown great potential for improving initial coulombic efficiency (ICE) by passivating rough surface structures and controlling the formation of the solid electrolyte interphase. To date, there is a lack of systematic studies on sucrose-coated hard carbon derived from walnut shells as an anode material for sodium-ion batteries. This master thesis aims to address this deficiency by synthesizing hard carbon derived from walnut shells and coating it with sucrose at different concentrations. A comprehensive comparative analysis of the structure and electrochemical performance of the coated and uncoated samples is carried out, and the results are compared with other biomass-derived hard carbon materials described in the literature. It is hoped that the results obtained will provide practical guidance for the development of low-cost anode materials with higher initial coulombic efficiency and greater cyclic stability.

Chapter Three: Methodology

3.1 Introduction

To reduce typical sodium losses in the first cycle of hard carbon anodes, it is necessary to seal the micropores and passivate the active surface areas. Conformal carbon coatings can inhibit electrolyte decomposition and stabilize the solid electrolyte interphase. In this study, sucrose was chosen as an economical, efficient, and readily available precursor capable of forming an amorphous carbon film on hard carbon derived from walnut shells after pyrolysis. The precursor preparation process (including mechanical milling, acid treatment, washing, pre-oxidation, and carbonization) is shown in Figure 4. The subsequent sucrose coating process (including solution preparation, mixing, ultrasonication, drying, and heat treatment at 600-750 °C) is shown in Figure 5. The electrode preparation process (including slurry preparation, melting, drying, electrode cutting, and half-cell assembly) is shown in Figure 6. The following methods describe: (1) the materials and reagents used; (2) synthesis of hard carbon from walnut shell; (3) preparation and coating of sucrose solutions of different concentrations to coat the hard carbon; (4) subsequent heat treatment to form a soft carbon layer; (5) evaluation of the structure and surface properties using characterization methods; and (6) flow diagram of electrode fabrication, battery assembly and electrochemical testing.

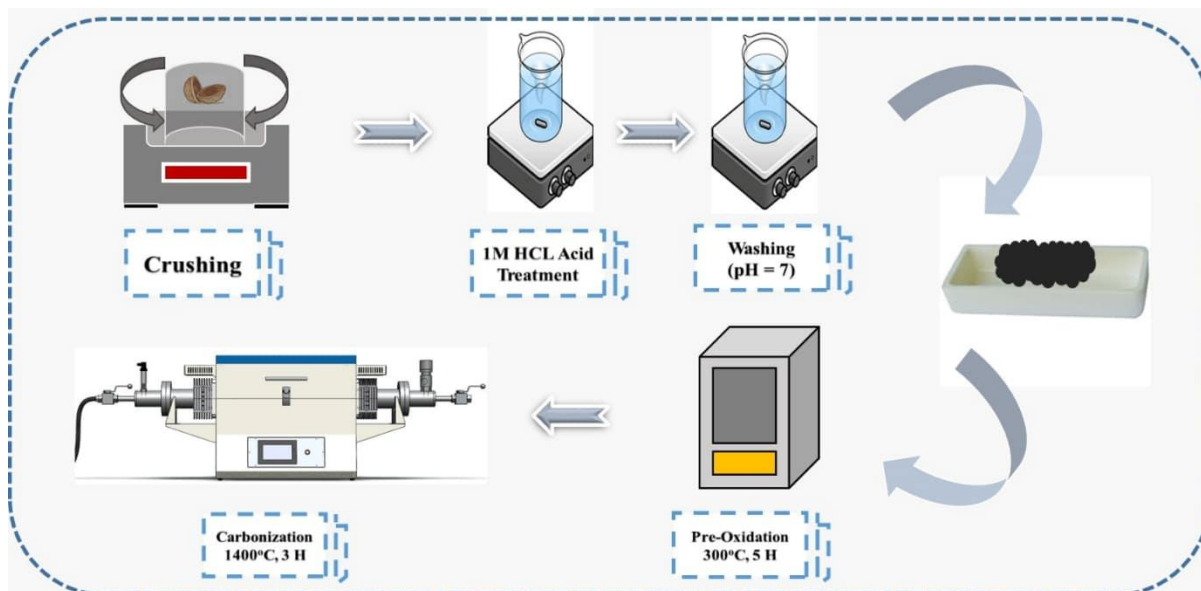


Figure 4. Overview of the fabrication procedure for converting biomass feedstock into hard carbon precursors suitable for sodium-ion battery anodes.

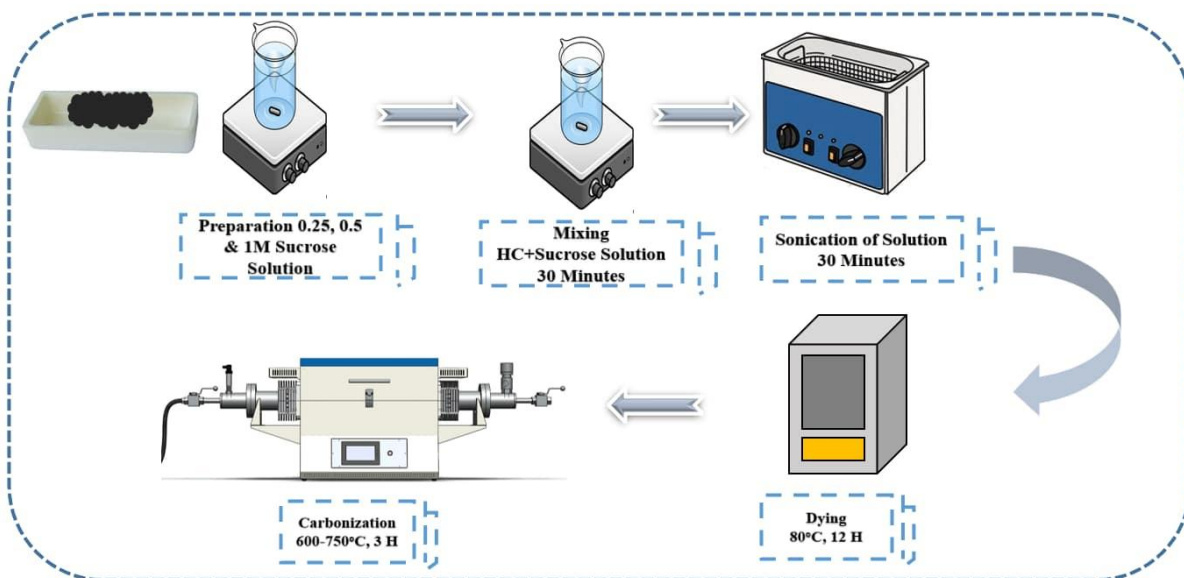


Figure 5. Sucrose Coating on Hard Carbon (HC) from Walnut Shell (WS)

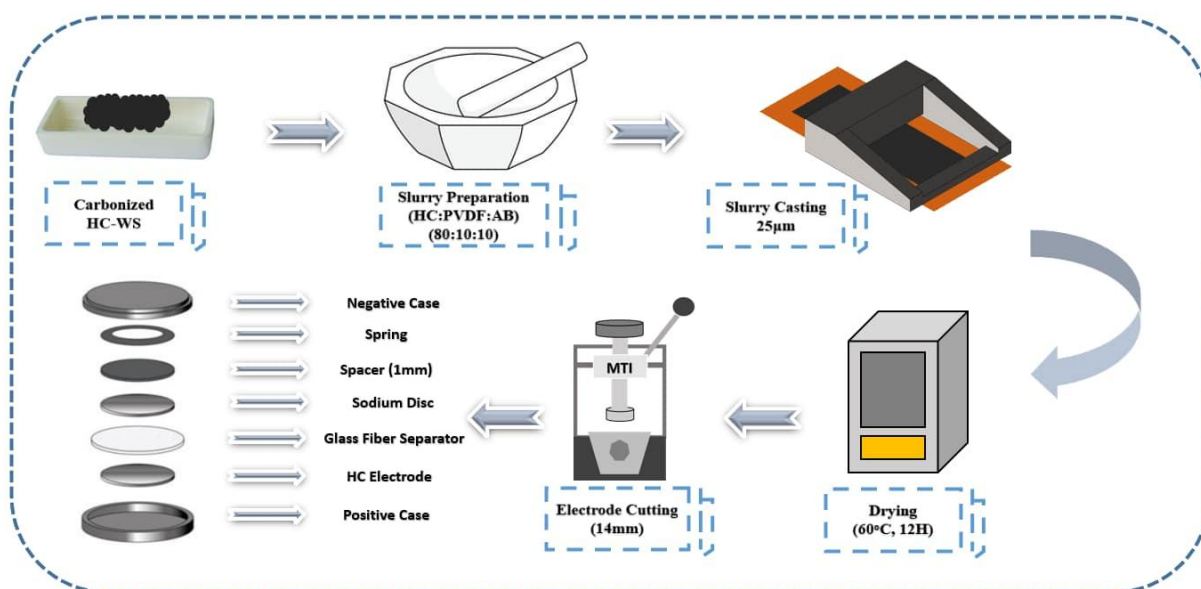


Figure 6. Electrode fabrication using HC-WS.

3.2 Materials and precursors

Walnut shells. In this study, dried walnut shells obtained from local food industry waste were used as biomass. To remove residual organic matter and minerals that could catalyze secondary reactions, the shells were first thoroughly washed with deionized water and then immersed in a 1 M hydrochloric acid solution. After washing to a neutral pH, they were dried at 80 °C for 24 hours. Walnut shells are a lignocellulosic biomass rich in cellulose, hemicellulose, and lignin; their carbonization produces a porous solid carbon matrix containing heteroatoms (O, N).

Sucrose (precursor for carbon coating). Analytical-grade sucrose was used as the soft carbon source. Aqueous sucrose solutions were prepared at concentrations of 0.25 M, 0.5 M, and 1 M. These solutions were added to hard carbon powder (obtained by carbonizing walnut shells at 1400 °C) to form a suspension. The mixture was stirred for 30 minutes, followed by ultrasonic treatment for 30 minutes to enhance the impregnation effect. After drying at 80 °C for 12 hours, the sucrose-coated hard carbon was carbonized at 600 °C for 3 hours under an argon atmosphere to form a thin amorphous carbon coating. This coating is designed to fill or encapsulate accessible micropores and passivate high-surface-area areas, thereby inhibiting SEI film growth and increasing the first-cycle coulombic efficiency. Sucrose was chosen as the coating precursor due to its wide availability, low cost, and clean thermal decomposition characteristics under inert atmospheric conditions, making it a particularly suitable material for the development of sustainable carbon coating strategies.

Table 3. Synthesis conditions and processing steps of solid carbon obtained from nut shells.

Sample number	Preprocessing stages-	solid carbon-	Sugar coating and pyrolysis
HC	1M HCl at 80°C for 2 hours; rinse until a neutral pH is reached; dry at 80°C for 24 hours.	Carbonization at 1400 °C. Maintain argon flow for 3 hours (heating rate 5 °C min ⁻¹).	(Without coating)
HC-0.25 M	Similar to HC	Similar to HC	Mix HC powder with 0.25 M sucrose solution; stir for 30 minutes; sonicate for 30 minutes; dry at 80 °C for 12 hours; pyrolyze at 600 °C for 3 hours in an argon atmosphere.
HC-0.5 M	Similar to HC	Similar to HC	HC powder with 0.5 M sucrose solution; Shake for 30 minutes; subject to ultrasound for 30 minutes; dry at 80°C for 12 hours; pyrolyze at 600°C for 3 hours in an argon atmosphere.

HC-1 M	Similar to HC (bare metal).	Similar to HC (bare metal).	Mix HC powder with 1M sucrose solution; stir for 30 minutes; sonicate for 30 minutes; dry at 80 °C for 12 hours; pyrolyze at 600 °C for 3 hours under argon.
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Table 4. List of materials and their application.

Chemical Material /	Formula	Brand / Source	Molecular Weight (g mol⁻¹)	Purity (%)	Application
Walnut shells (biowaste)	-	Local source	-	-	Hard carbon precursor
Hydrochloric acid	HCl (1M)	Sigma-Aldrich	36.46	AR grade	Pretreatment of biowaste precursors
Distilled water	H ₂ O	Laboratory grade	-	-	Solvent for precursor dissolution and washing
Ethanol, anhydrous	C ₂ H ₅ OH	Sigma-Aldrich	46.07	99.5	Solvent for washing and slurry preparation
Acetone	C ₃ H ₆ O	Sigma-Aldrich	58.08	99	Cleaning and electrode processing
Polyvinylidene fluoride (PVDF)	(C ₂ H ₂ F ₂) _n	MTI Corp	64.03	-	Binder for electrode slurry
N-methyl-2-pyrrolidone (NMP)	C ₅ H ₉ NO	Sigma-Aldrich	99.13	99	Solvent for PVDF binder
Copper foil	Cu	MTI Corp	-	-	Anode current collector

Sodium metal cubes	Na	Sigma	22.99	99	Counter/reference electrode in half-cells
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3.3 Synthesis of hard carbon and sucrose coatings

Acid-washed and dried walnut shells were mechanically ground to a coarse powder with a particle size of approximately 2-5 mm. Approximately 10 g of this coarse powder were placed in a high-temperature tubular furnace with continuous argon purging. The furnace temperature was raised from ambient temperature to 1400 °C at a rate of 5 °C min⁻¹ and held at 1400 °C for 3 hours, followed by natural cooling to ambient temperature under an argon atmosphere. The carbonization product was collected, mechanically ground, and sieved to obtain a finely dispersed solid carbon powder with a uniform particle size distribution. Sucrose impregnation. Aqueous sucrose solutions were prepared at concentrations of 0.25 M, 0.5 M, and 1 M. Solid carbon powder was mixed with the sucrose solution in a solid-to-liquid ratio that thoroughly wetted the powder. The suspension was stirred with a magnetic stirrer for 30 minutes, followed by ultrasonic treatment for 30 minutes to enhance sucrose penetration into the porous structure. After impregnation, the suspension was dried at 80 °C for 12 hours to remove moisture. The dried sucrose-coated powder was carbonized at 600 °C for 3 hours under an argon atmosphere to convert the sucrose into a thin coating of amorphous carbon.

Samples coated with 0.25 M, 0.5 M, and 1 M sucrose solutions were designated HC-0.25M, HC-0.5M, and HC-1M, respectively. Uncoated hard carbon samples (designated HC) were subjected to the same high-temperature carbonization process, but the sucrose impregnation and 600 °C coating steps were omitted.

3.4 Materials for the production of electrodes

The working electrode was fabricated using the solid carbon powder synthesized in Section 3.3 (including pure solid carbon powder and sucrose-coated samples). Its composition and fabrication technology followed the established procedures for sodium-ion battery anodes:

- Active ingredient: Before use, carefully grind the solid carbon powder (HC or HC-S) in an agate mortar to break up any clumps.
- Conductive additives. Acetylene black (AB) is used as a conductive carbon to provide penetration pathways in the electrode film.

- Adhesive. Polyvinylidene fluoride (PVDF) (Solef5130) was used as the polymeric adhesive. PVDF has good chemical stability against sodium salts and is capable of forming films with good adhesion.
- Solvent. PVDF is dissolved in N-methylpyrrolidone (NMP) to ensure uniform distribution of the active material and AB.
- Current collector. All anode membranes use a copper sheet (10 μm) as a current collector.

A composite suspension was prepared by mixing the active materials, acetylene black and PVDF, in a weight ratio of 80:10:10. The powders were first dry-mixed -to ensure homogeneity and then dispersed in NMP to form a viscous suspension. The resulting suspension was applied to a copper sheet using a spatula to ensure a uniform thickness of the wet film on the substrate. The coated copper sheet was vacuum-dried at 80 °C for 12 hours to completely remove the solvent. After drying, circular electrode plates approximately 14 mm in diameter were obtained by mechanical stamping for use in disc cells.

3.5 Characterization methods

The synthesized carbon materials were examined through multiple complementary analytical methods to evaluate their structural, morphological, surface chemical, and electrochemical characteristics. Crystal structure and interlayer spacing were investigated via X-ray diffraction (XRD) employing Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The extent of structural disorder and graphitic ordering was probed using Raman spectroscopy with a 514.5 nm excitation laser. Surface morphology was examined by scanning electron microscopy (SEM), while internal nanostructural features and the formation of the sucrose-derived coating layer were verified through transmission electron microscopy (TEM). Elemental composition and spatial distribution were mapped using energy-dispersive X-ray spectroscopy (EDS) coupled with SEM. Surface chemical states and the nature of functional groups were identified by X-ray photoelectron spectroscopy (XPS). Constant current charge-discharge (GCD) tests were used to characterize the electrochemical properties of the material, including specific capacitance, initial coulombic efficiency, cycle stability, and charge/discharge rate characteristics. Subsequently, differential capacitance (dQ/dV) curves were constructed from the GCD data to better understand the sodium ion storage mechanism in the synthesized material.

Table 5. Summary of the different characterization methods.

Technique	Tools/Terms	Information received
X-ray diffraction (XRD)	Bruker D8 (Cu K α , 40 kV, 40 mA, $2\theta = 10-80^\circ$)	Determine the crystalline structure, the spacing between layers (d002) and the ordering of graphite in carbon materials.
Raman spectroscopy	Thermo DXR, 532 nm laser, 800-2000 cm ⁻¹	The degree of structural disorder and graphitization was assessed using D and G band analysis.
Scanning electron microscope (SEM)	Jeol JSM-7600F, 5-10 kV	Study the surface morphology, grain size, and texture of the carbon material.
Transmission electron microscopy (TEM)	FEI Tecnai G2, 200 kV	It provides information about the nanostructure, including the arrangement of layers and the characteristics of the coating.
Energy-dispersive X-ray spectroscopy (EDS)	Integration with scanning electron microscopy/transmission electron microscopy systems.	Determine the elemental composition and spatial distribution of the elements.
X-ray photoelectron spectroscopy (XPS)	Kratos Axis Supra (Al K α radiation)	Analyze the chemical composition of the surface and identify the functional groups present on the carbon surface.
Charge-Discharge (GCD) and Derived Electrochemical Analysis	Neware battery testing system	Evaluate electrochemical performance, including specific capacity, initial coulombic efficiency (ICE), cycle stability, rate characteristics, and differential capacitance (dQ / dV) behavior.

3.6 Electrode Preparation

Before assembling the electrodes, the hard carbon active material underwent vacuum drying at 120 °C for 2 hours to eliminate any remaining moisture. To prepare the electrode slurry, hard carbon, acetylene black (AB), and polyvinylidene fluoride (PVDF) were combined in a mass ratio of 80:10:10. The dry constituents were thoroughly blended prior to the gradual introduction of N-methyl-2-pyrrolidone (NMP), which served as the dispersing medium to produce a viscous, uniform slurry. This slurry was then cast onto a copper current collector using a spatula, achieving a consistent film thickness across the substrate surface. The resulting electrode film was subsequently placed under vacuum at 80 °C for a minimum of 12 hours to fully remove the solvent. Circular electrode discs of approximately 14 mm in diameter were then punched from the dried copper-coated sheet using a mechanical stamp. The mass loading of active material was carefully controlled to fall within the 1.0-1.5 mg cm⁻² range. Prior to cell assembly, the electrode discs underwent an additional drying step at 110 °C under vacuum for 2 hours and were subsequently stored in an argon-purged drying cabinet to avoid any exposure to ambient humidity and oxygen.

3.7 Coin cell assembly and electrochemical testing

Electrochemical characterization was carried out using CR2032 coin-type half-cells, assembled inside a glove box maintained under argon atmosphere with both oxygen and water vapor levels kept below 0.1 ppm. Either uncoated hard carbon (HC) or sucrose-impregnated hard carbon (HC-S) served as the working electrode, while metallic sodium acted as both the counter and reference electrode. A fiberglass membrane was employed as the separator, and 1 M NaPF₆ dissolved in a mixed solvent of ethylene carbonate (EC) and diethyl carbonate (DEC) was used as the electrolyte. Following assembly, cells were left to rest for sufficient time to allow complete electrolyte infiltration into the electrode structure. Galvanostatic charge-discharge measurements were then conducted at room temperature on a Neware battery tester over a potential window of 0.01-2.5 V vs. Na⁺/Na. The initial coulombic efficiency (ICE) was derived from the first cycle at low current density, promoting stable and uniform SEI layer formation. Long-term cycling stability and rate capability were subsequently assessed at elevated current densities, with stepwise increases in current used to evaluate sodium-ion diffusion kinetics and electrode durability under varying charge-discharge conditions.

Chapter 4. Results and discussion.

4.1 X-ray diffraction analysis of solid carbon

X-ray diffraction (XRD) was used to evaluate the effect of the sucrose coating on the structural order and interlayer spacing of the hard carbon samples, two key parameters that determine sodium ion storage efficiency. The diffraction patterns of all samples (Fig. 7) showed broad rather than sharp diffraction peaks, indicating a predominantly amorphous structure containing layered, graphene-like disordered regions. Two characteristic peaks were identified in the diffraction patterns: a broad peak in the 22-25° range, attributed to the (d_{002}) crystal plane; and a weaker diffraction peak near 43°, associated with the in-plane correlation of the (100)/(101) crystal plane. The broad peaks and their low intensity are consistent with the disordered packing characteristics of the graphene layers in the biomass-derived hard coal.

Quantitative analysis of the (d_{002}) reflection revealed that sucrose impregnation appreciably modified the interlayer distance (d_{002}), as shown in Table 6. The d_{002} value increased from 3.808 Å in unmodified HC to 3.904 Å in the 0.25 M sample, signifying an expansion of the interlayer spacing anticipated to facilitate Na⁺ intercalation. At higher sucrose concentrations (0.5M and 1M), d_{002} decreased to 3.529Å and 3.554Å, respectively, indicating the onset of partial structural densification. Furthermore, after sucrose treatment, the grain height (L_c) and number of layers (N) increased significantly: from 9.9Å (approximately 3 layers) in pure hard carbon (HC) to 18.2-22.3 Å (approximately 5-6 layers) in the coated samples, indicating greater stacking coherence and the emergence of sucrose-derived carbon domains. The full width at half height (FWHM) values confirm this trend; compared to pure HC, the FWHM values in the sucrose-treated samples decreased, reflecting greater structural coherence. However, at high sucrose concentrations, the increased FWHM indicates that the coating induces structural heterogeneity and altered order.

Overall, the X-ray diffraction results show that sucrose impregnation balances the relationship between increased interlayer spacing and improved layer ordering. Treatment with a moderate concentration (0.25 M) ensures an optimal structural configuration, combining the benefits of increased interlayer spacing and greater layer stability, while higher concentrations lead to structural disorder. Notably, no clear graphite peaks were observed in any of the samples, confirming the absence of complete graphitization and the preservation of the disordered layer structure necessary for efficient sodium storage in hard carbon anodes in all materials.

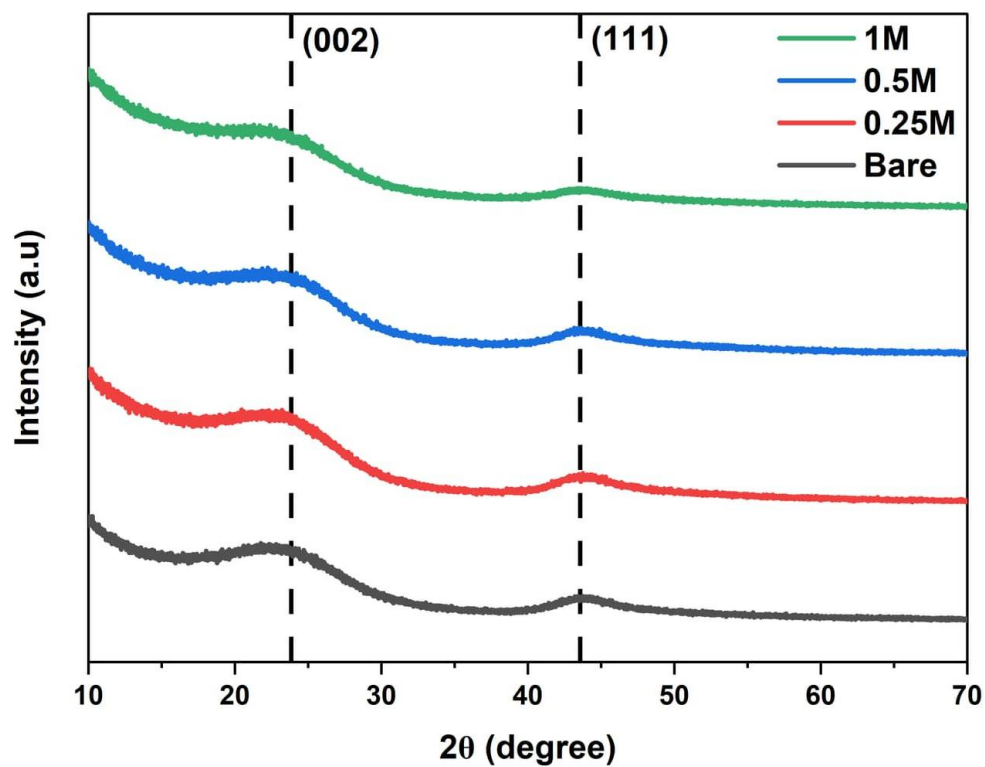


Figure 7. The X-ray diffraction patterns of the HC and HC-S samples demonstrate the general characteristics of disordered lamellar solid carbon.

Table 6. XRD-derived structural parameters for HC and HC-S

sample	2θ (degrees)	d_{002} Å	FWHM (degrees)	L_c (Å)	N (layers)
Bare	23.34	3,808	8.10	9.9	3
0.25M	22.76	3,904	6.20	22.3	6
0.5M	25.22	3,529	6.84	20.6	6
1.0M	25.03	3,554	7.78	18.2	5

4.2 Raman spectroscopic analysis of solid carbon

Raman spectroscopy was employed alongside XRD to further probe local structural defects and disorder within the carbon framework, both of which critically govern sodium-ion storage behavior. All samples exhibited two well-defined peaks (Fig. 8): a D band near 1350 cm^{-1} and a G band in the $1580\text{--}1600\text{ cm}^{-1}$ range, consistent with the dominance of sp^2 -hybridized carbon. The D band originates from disorder-induced vibrational modes at edge sites and lattice vacancies, whereas the G band reflects in-plane stretching of sp^2 carbon atoms within graphitic regions. The broad nature of both peaks across all samples confirms the preservation of a turbostratic, disordered carbon architecture rather than a well-ordered graphitic one, in good agreement with XRD findings. Quantitative evaluation of the $I_{\text{D}}/I_{\text{G}}$ intensity ratio revealed a systematic decrease following sucrose impregnation — from 1.10 in the untreated HC to 0.858, 0.89, and 0.95 for the 0.25 M, 0.5 M, and 1 M treated samples, respectively. This progressive reduction reflects a gradual enhancement in graphitic ordering and a decline in overall defect concentration. The trend indicates that the sucrose-derived carbon layer facilitates the development of more ordered sp^2 domains while retaining adequate defect sites to support reversible sodium-ion accommodation. Notably, the 0.25 M sample exhibited the lowest ratio between I_{D} and I_{G} of all coated samples, demonstrating an optimal balance between structural ordering and defect retention. The in-plane grain size (L_a) provides further information, decreasing from approximately 21.1 nm in pure hard carbon (HC) samples to 16.5–18.2 nm in sucrose-treated samples. This decrease indicates that sucrose impregnation introduces additional nanoscale domains and defect sites that can serve as active adsorption sites for Na^+ while maintaining electronic conductivity through interconnected graphitic domains. Overall, Raman spectroscopy results confirm that sucrose impregnation effectively modulates the carbon microstructure, simultaneously enhancing the short-range order of graphite and introducing controlled defects. Treatment at a moderate concentration (0.25 M) ensures optimal structural equilibrium, which is expected to promote the accumulation of adsorbed sodium and the formation of a stable SEI film. At higher sucrose concentrations, increased structural disorder and possible oxygen incorporation can alter the graphite domains, consistent with observations obtained from X-ray diffraction analysis and electrochemical characterization.

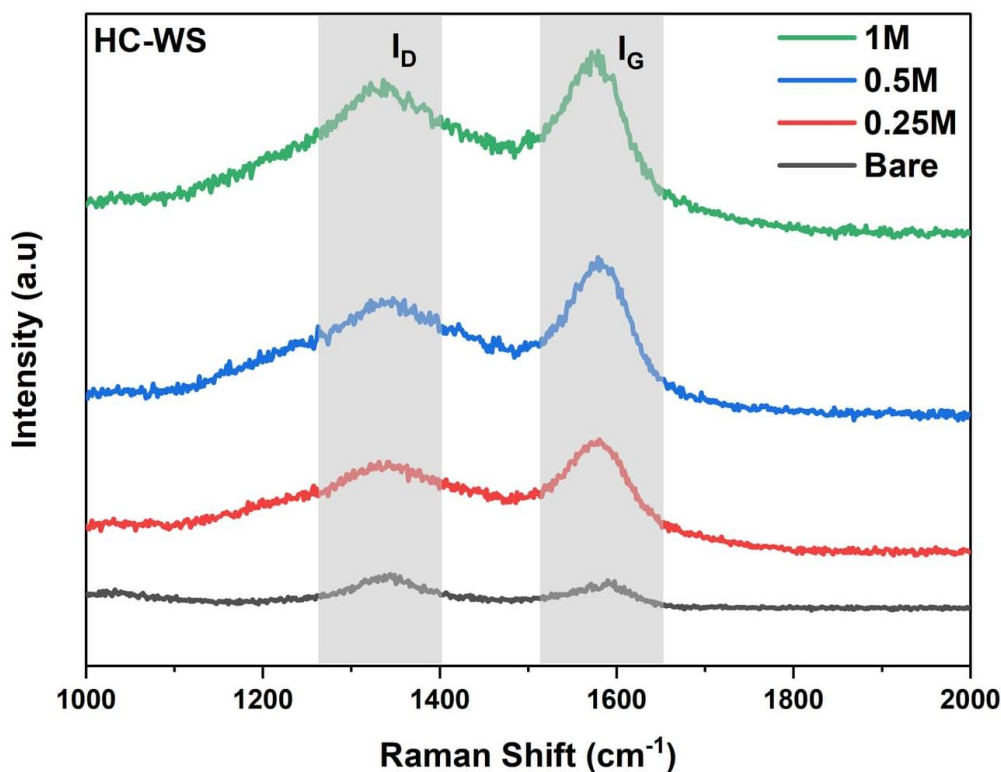


Figure 8. Raman spectra of hard carbon derived from walnut shell (HC-WS) and sucrose-coated samples, showing the D and G bands.

4.3 Morphological analysis of solid carbon using SEM and TEM

Scanning electron microscopy (SEM) images (Fig. 9) show the effect of sucrose coating on the surface morphology of hard carbon derived from walnut shells. Figure (a) shows a sample of pure hard carbon consisting of irregular, flake- and block-like particles with numerous fracture edges and open micropores. These morphological features are typical of biomass-derived hard carbon and result from the heterogeneity of the lignocellulosic precursor and the development of porosity during high-temperature pyrolysis. After impregnation with a 0.25 M sucrose solution (Fig. (b)), the particle surface became significantly smoother, with numerous sharp edges and open pores covered by a thin layer of soft coal obtained from sucrose pyrolysis. This conformal coating effectively reduced the size and number of accessible pores. Among all the samples, the one treated with 0.5 M sucrose solution (Fig. (c)) exhibited the most uniform surface morphology, with pores and surface defects effectively sealed, resulting in a dense and continuous particle surface appearance. In contrast, the coating with 1 M sucrose solution (Fig. (d)) formed a significantly thicker layer of amorphous carbon, resulting in almost complete pore filling and a glassy, highly aggregated particle surface morphology. These scanning electron microscopy observations are consistent with the role of sucrose-derived carbon as a

surface passivation layer. The gradual surface smoothing and pore closure observed in Figure 9 indicate that sucrose-derived carbon is preferentially deposited on the outer surface of the particles and in the pore openings, thereby reducing the number of exposed sharp edges, partially blocking accessible pores, and minimizing direct contact between the electrolyte and defect-rich surface regions. This physical sealing mechanism is postulated to suppress excessive solid electrolyte interphase (SEI) formation, thereby increasing the initial coulombic efficiency (ICE). However, it should be noted that, due to the limited contrast between carbon phases under electron imaging conditions, scanning electron microscopy (SEM) alone is insufficient to accurately determine coating thickness or structural continuity. Therefore, additional characterization methods, such as high-resolution transmission electron microscopy (TEM), are required to definitively confirm the core-shell arrangement of the coated particles.

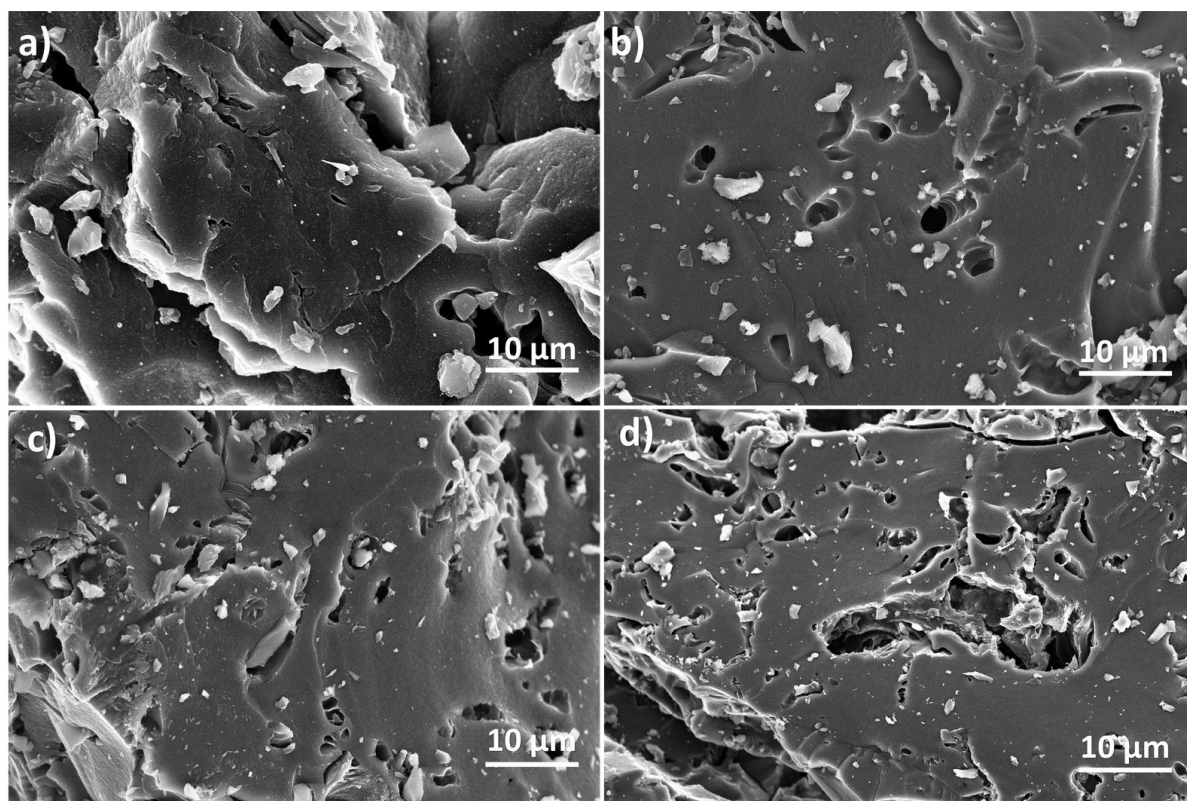


Figure 9. SEM micrographs of walnut-shell hard carbon (HC) and sucrose-coated hard carbon (HC-S) powders: (a) Bare, (b) 0.25 M coated, (c) 0.5 M coated, (d) 1 M coated.

Transmission electron microscopy (TEM) was further employed to examine the nanoscale structural features of all prepared samples (Fig. 10). For pure hard carbon (HC) (Fig. a), the carbon exhibits a disordered, layered structure consisting of short, curved, graphene-like layers with no long-range spacing. The absence of the distinctive parallel lattice bands typical of graphitic carbon confirms its nature as hard carbon rather than a transformation to highly

crystalline graphite. The 0.25 M coated sample (Fig. b) shows a similar disordered core but with a slightly smoother surface, indicating the deposition of a thin sucrose-derived layer. In the 0.5 M sample (Fig. c), a thin, relatively uniform, amorphous coating a few -nanometers thick surrounds the disordered core, indicating that this coating concentration forms a conformal layer of soft carbon. The 1 M sample (Fig. d) shows a darker, thicker amorphous layer surrounding the particles, indicating a thicker coating that, if too thick, can impede Na^+ diffusion. Overall, transmission electron microscopy (TEM) images confirmed that the sucrose coating did not induce graphitization; all samples retained the -disordered, layered structure of the hard carbon with nanoscale disorder. The soft carbon derived from sucrose formed a thin, uniform layer whose thickness increased with the solution concentration. This model of a disordered carbon core structure with a thin amorphous layer is consistent with the X-ray diffraction and Raman spectroscopy results and explains the improvement in initial Coulombic efficiency and cyclic stability observed in the better-coated samples.

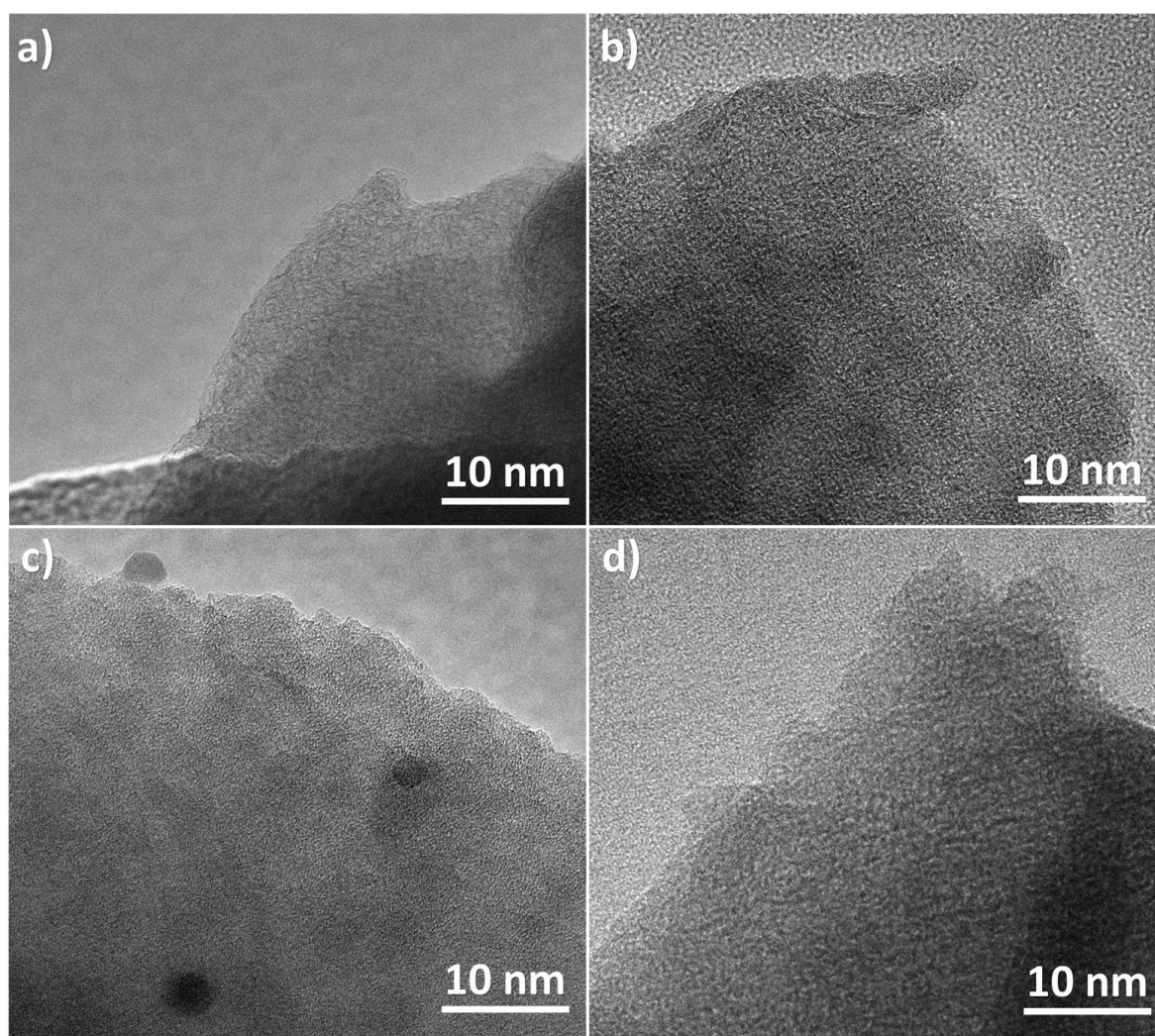


Figure 10. TEM micrographs of HC and HC-S: (a) Bare, (b) 0.25M, (c) 0.5M, (d) 1M.

4.4. Galvanostatic charge-discharge test for hard carbon

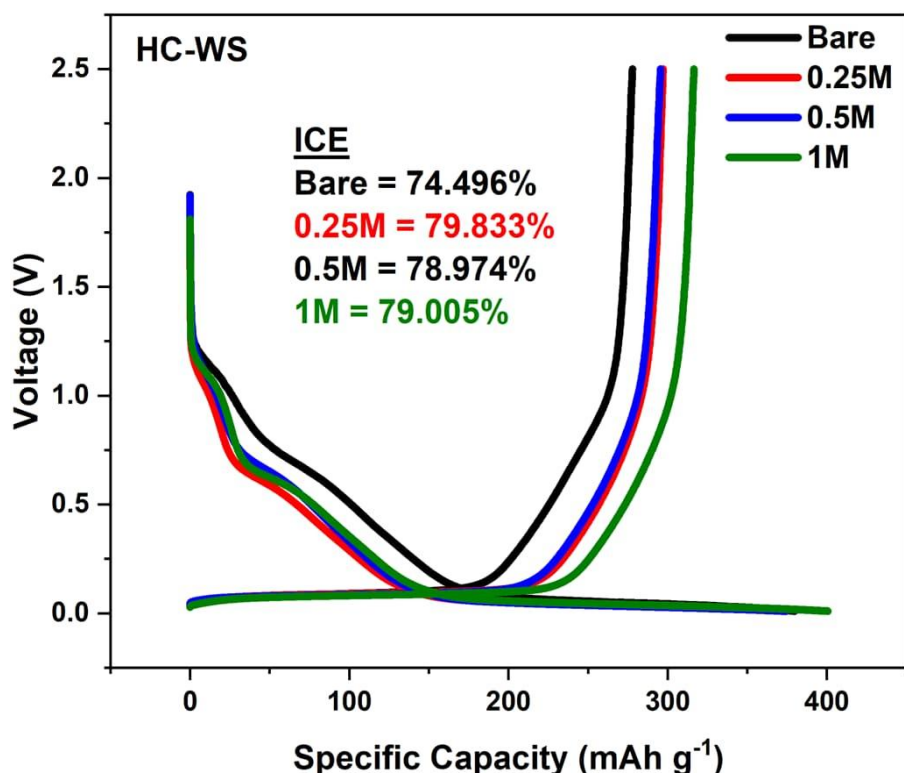


Figure 11. First-cycle galvanostatic charge-discharge profiles of HC-WS and sucrose-coated samples showing improved initial Coulombic efficiency (ICE)

Constant current measurements (Figure 11) showed the typical sodium ion storage behavior of hard carbon, characterized by a sloping curve in the high-voltage region (~ 2.0 - 0.1 V) followed by a plateau at low voltage below 0.1 V. The pure hard carbon electrode had a high initial sodium storage capacity close to 400 mAh g^{-1} ; however it exhibited significant irreversible capacity loss during the first cycle, resulting in an initial coulombic efficiency (ICE) of only 74.496%. This phenomenon is attributed to the large specific surface area and abundance of defective sites in uncoated hard carbon, which promoted intense electrolyte decomposition and the formation of a solid electrolyte interphase (SEI), thereby consuming large amounts of sodium ions. Compared to pure hard carbon, all sucrose-coated samples exhibited superior electrochemical reversibility, as reflected in an increased ICE value (Figure 11). Compared to pure hard carbon (HC) with a value of 74.496%, the HC-0.25M sample achieved the highest initial coulombic efficiency (ICE) of 79.833%, followed by HC-0.5M (78.974%) and HC-1M (79.005%). These improvements indicate that the sucrose-derived carbon coating effectively enhances the surface properties of the hard carbon anode. Furthermore, the voltage profile of the coated samples also changed significantly, particularly in the sloping region, exhibiting a

steeper slope than that of pure hard carbon. This suggests that the surface modification alters the sodium accumulation behavior in this voltage range. The improved ICE can be attributed to the formation of a thin coating of amorphous carbon, which passivates the surface sites rich in defects and reduces direct contact between the electrolyte and the carbon surface. Furthermore, the partial sealing of accessible surface micropores reduces the electrochemically active surface area, thus limiting excessive SEI film formation and minimizing irreversible sodium consumption during the initial cycle. While the HC-1M sample exhibits a relatively wide plateau region at low voltage and high reversible capacity, excess sucrose can lead to the formation of an excessively thick carbon coating layer, hindering Na^+ transport and reducing kinetic performance. In contrast, the HC-0.25M sample offers the best balance between surface passivation and ion transport availability, demonstrating the best electrochemical performance in the first cycle among the samples studied.

4.5 Cyclic stability of solid hard carbon

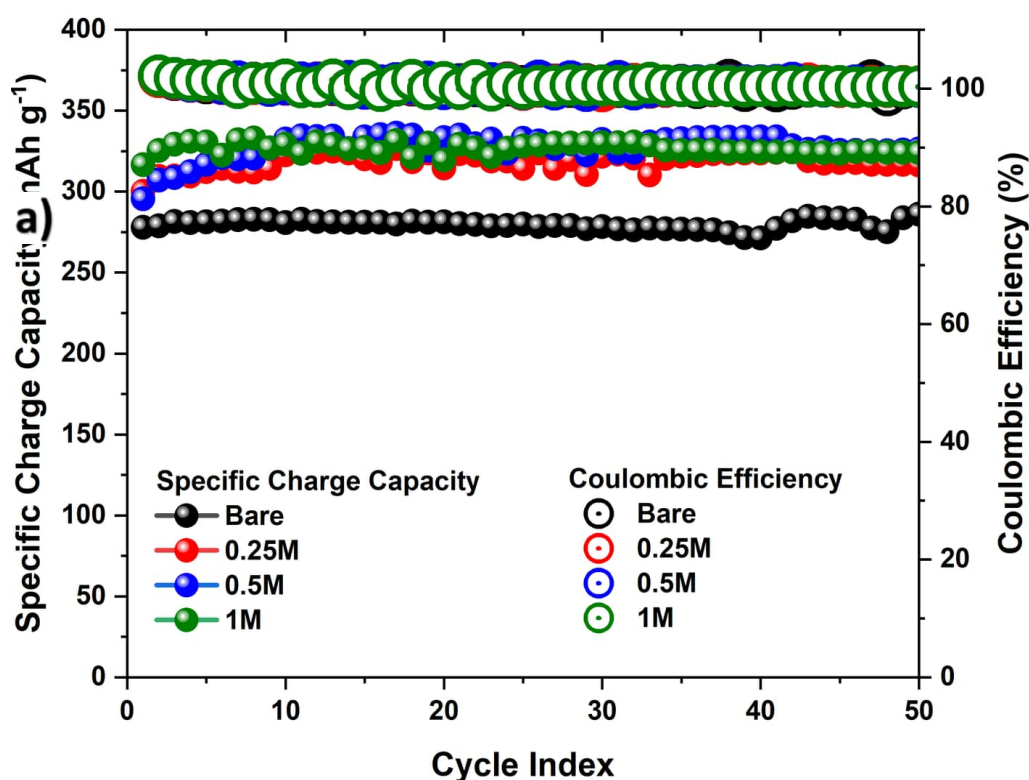


Figure 12. Comparative cycling stability

Figure 12 compares the long-term cycling performance of -uncoated and sucrose-coated walnut shell electrodes. Figure 12 shows the specific discharge capacity curves after 50 cycles at a constant current density. The uncoated walnut shell electrode exhibits a relatively stable but low reversible capacity, stabilizing at around 280 mAh g^{-1} . This limited capacity and slight

decrease reflect the irreversible consumption of sodium ions during the formation of a thick SEI film on the highly porous, defect-rich surface of the uncoated carbon material. In contrast, all sucrose-coated electrodes exhibit significantly higher and more stable capacities, confirming that the soft carbon layer prevents further SEI film formation and protects the sodium ions. Among all the modified samples, the HC 0.25M electrode exhibited the best capacity retention: its capacity stabilized at around 330 mAh g⁻¹ and it retained more than 95% of its initial capacity after 50 cycles. The HC 0.5M and HC 1M electrodes also outperformed the bare carbon electrode, but with slightly lower capacities (approximately 315-325 mAh g⁻¹) and less capacity degradation during long-term cycling. Furthermore, the coulombic efficiency of each electrode was monitored as a function of the number of cycles. The uncoated HC electrode showed lower efficiency and worse stability in the first few cycles, indicating persistent side reactions and SEI film growth. In contrast, the sucrose-coated electrode quickly reached almost 100% coulombic efficiency in the first few cycles and maintained this value for 50 cycles. It is worth noting that the HC 0.25M sample reached nearly 100% efficiency more quickly and remained more stable, further confirming that an appropriate amount of sucrose coating can provide an optimal balance between surface passivation and ion transport. Thicker coatings (0.5-1 M) also increased efficiency but increased the thickness of the soft carbon layer, which slightly increased impedance and reduced long-term capacity retention. Overall, the results of these two comparisons demonstrate that sucrose impregnation significantly improves cycle stability and reversibility by suppressing the continued growth of the SEI membrane and minimizing irreversible sodium ion loss. A moderate sucrose concentration (0.25 M) is ideal for maintaining high capacity and near-perfect coulombic efficiency, while both no coating and excessively thick coatings (1 M) lead to long-term performance degradation.

4.6 Rate Capability of hard carbon

Figure 13 shows the charging capacity and coulombic efficiency of hard walnut shell carbon electrodes at different current densities compared to the untreated electrode treated with different sucrose concentrations (0.25 M, 0.5 M, and 1 M). The untreated carbon electrode exhibited low initial coulombic efficiency and poor velocity characteristics, associated with a limited number of closed micropores and unstable surface chemistry. In contrast, the sucrose-treated sample showed significantly improved performance, especially at medium concentrations. The 0.25 M sucrose treatment conditions proved optimal. The initial coulombic efficiency of this treated sample was approximately 80%, which is significantly higher than that of the untreated electrode, and it maintained stable capacity after prolonged charging and

discharging cycles. Even with a gradual increase in current density (from 20 mA g⁻¹ to 2000 mA g⁻¹), the electrode treated with a 0.25 M sucrose solution demonstrated excellent performance at different charge and discharge rates, and the capacity was restored when the current density returned to 20 mA g⁻¹. This phenomenon highlights the effectiveness of the soft carbon layer formed during sucrose pyrolysis, which enhances ion transport pathways while maintaining structural order. At higher sucrose concentrations (0.5 M and 1 M), the electrode's performance remained superior to that of untreated carbon, but its long-term stability decreased. Excessive sucrose decomposition led to structural defects and increased oxygen content, which hampered electronic conductivity and reduced coulombic efficiency during cycling. This trade-off underscores the importance of balancing defect control and conductivity in biomass-derived carbon materials. Overall, electrochemical trends confirm that moderate sucrose treatment can improve sodium ion storage by forming additional closed pores, increasing interlayer spacing, and stabilizing the solid electrolyte interphase (SEI). The sample at a concentration of 0.25 M demonstrated the best combination of structural integrity, defect control, and conductivity, making it the most promising material for practical applications in sodium-ion batteries.

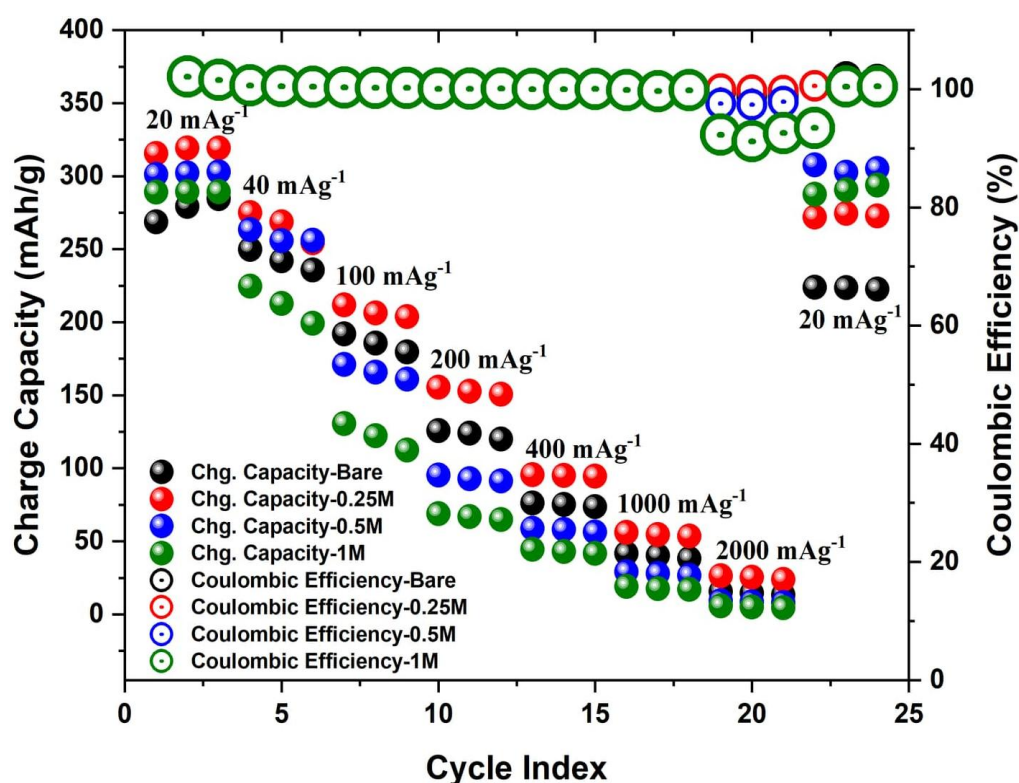


Figure 13. Rate Capability of HC-WS and sucrose-treated electrodes

4.7 Analysis of the differential capacity of solid carbon

To further elucidate the sodium ion storage mechanism in the synthesized materials, we performed a differential capacitance (dQ/dV) analysis (Fig. 14). The dQ/dV curves of all samples exhibited a pair of pronounced redox peaks at low voltages, including a cathodic peak below approximately 0.1 V and a corresponding anodic peak around approximately 0.1 V (vs. Na^+/Na). These features are typical of the plateau region of hard carbon and are generally attributed to reversible sodium ion storage in closed pores or nanopores. Significant differences in peak intensity were observed among the samples; the low-voltage peak intensity of the sucrose-coated material was higher than that of pure hard carbon, indicating a greater reversible sodium ion storage capacity in the plateau region. In particular, the HC-0.5M sample exhibited the most significant low-voltage peak, suggesting a greater contribution from the pore-filling storage mechanism in this sample. In contrast, the pure carbon material exhibited weaker peaks in the low-voltage region, while a more pronounced broad cathodic peak ($\sim 0.5\text{-}1.0$ V vs. Na^+/Na) was observed in the high-voltage region. This broad peak is typically associated with irreversible electrochemical processes, including electrolyte decomposition and SEI layer formation in defect-rich surface regions. The reduced intensity of this peak in the coated samples indicates that sucrose treatment effectively suppressed these side reactions. The difference in the dQ/dV curves can be explained by the effect of the sucrose-derived carbon coating, which modifies the carbon surface, partially passivating defective sites and limiting direct electrolyte access to open pores. Consequently, irreversible electrochemical reactions are minimized, and more sodium ions participate in reversible storage within the carbon structure. Overall, the dQ/dV analysis results are consistent with the constant current charge-discharge results, demonstrating that the sucrose coating enhances the reversible accumulation of sodium ions while suppressing irreversible side reactions. Among all the samples studied, HC-0.5M provides the optimal balance between these two mutually limiting factors, confirming its excellent performance in charge-discharge cycles.

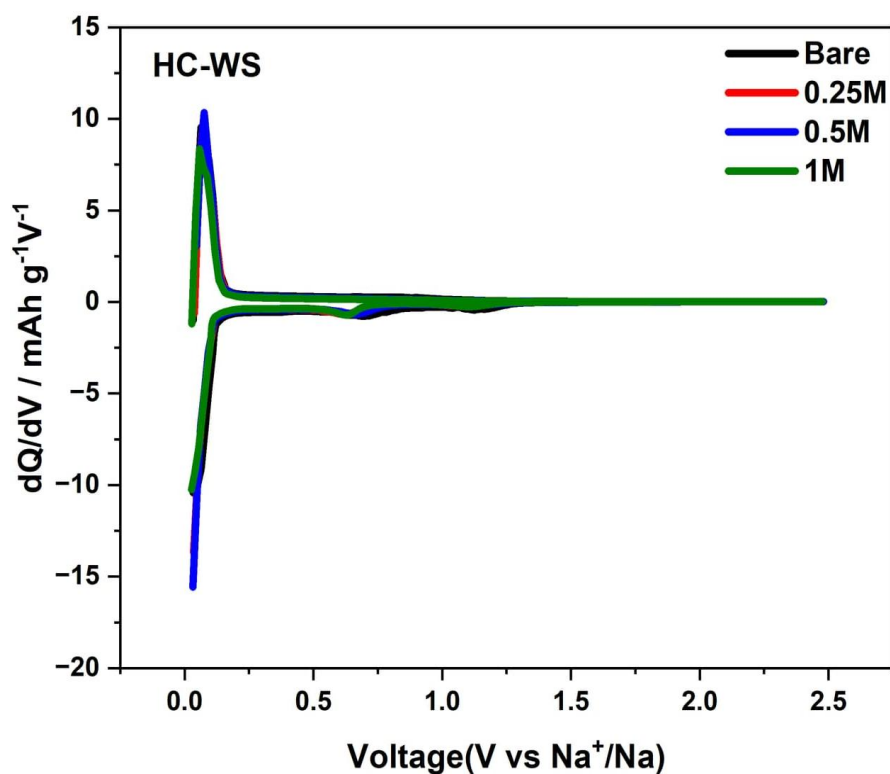


Figure 14. Differential capacity (dQ/dV) curves of HC-WS and sucrose-coated samples showing sodium storage behavior.

4.8 Analysis of surface chemical properties by X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was utilized to examine the surface chemical composition and bonding characteristics of both uncoated and sucrose-treated hard carbon samples (Fig. 15). Survey spectra (Fig. 15c, f, i, l) revealed that all samples consisted predominantly of carbon and oxygen, reflected by prominent C1s and O1s signals. Notably, the O1s signal intensity showed a progressive decline across the sample series with increasing sucrose concentration, suggesting that the impregnation and subsequent pyrolysis systematically lowered the surface oxygen content. High-resolution C1s spectra (Fig. 15a, d, g, j) provided further insight into the surface bonding environment. Spectral deconvolution identified a primary peak at approximately 284.8 eV, assignable to sp^2 -hybridized C-C/C=C bonds, along with secondary contributions at higher binding energies (~ 286 eV and ~ 288.5 eV), corresponding to oxygen-bearing functional groups including C-O, C=O, and O-C=O species. In the HC samples, a relatively significant contribution of high-bond-energy components was observed, reflecting the abundance of oxygen-containing functional groups and structural defects on their surface. Following sucrose coating, the C1s spectra of the

modified samples gradually became dominated by C-C bond-associated components, while the contribution of oxygen-containing functional groups progressively decreased. This change in surface chemical composition indicates that the sucrose-derived carbon coating effectively reduced the relative abundance of reactive oxygen-containing functional groups on the carbon surface. A similar trend was observed in the corresponding O1s spectra (Fig. 15b, e, h, k), where the number and intensity of oxygen-related spectral components decreased significantly compared to the uncoated hydrocarbons (HCs). These surface chemical modifications have a significant impact on electrochemical performance. Oxygen-containing functional groups are known to participate in irreversible side reactions during the initial charge-discharge cycles, leading to excessive sodium consumption and the formation of excess SEI layers. Therefore, reducing the number of these active surface sites in sucrose-coated samples is expected to suppress irreversible electrochemical processes and increase the initial coulombic efficiency. In conclusion, the X-ray photoelectron spectroscopy (XPS) results show that the sucrose coating systematically alters the surface chemical composition of the hard carbon derived from walnut shells, reducing the relative proportion of oxygen-containing functional groups and increasing the proportion of carbon-carbon bonds. This chemical passivation effect, combined with the structural and morphological changes revealed by X-ray diffraction (XRD), Raman spectroscopy, and scanning electron microscopy (SEM), contributes to the improved electrochemical performance of the sucrose-coated samples.

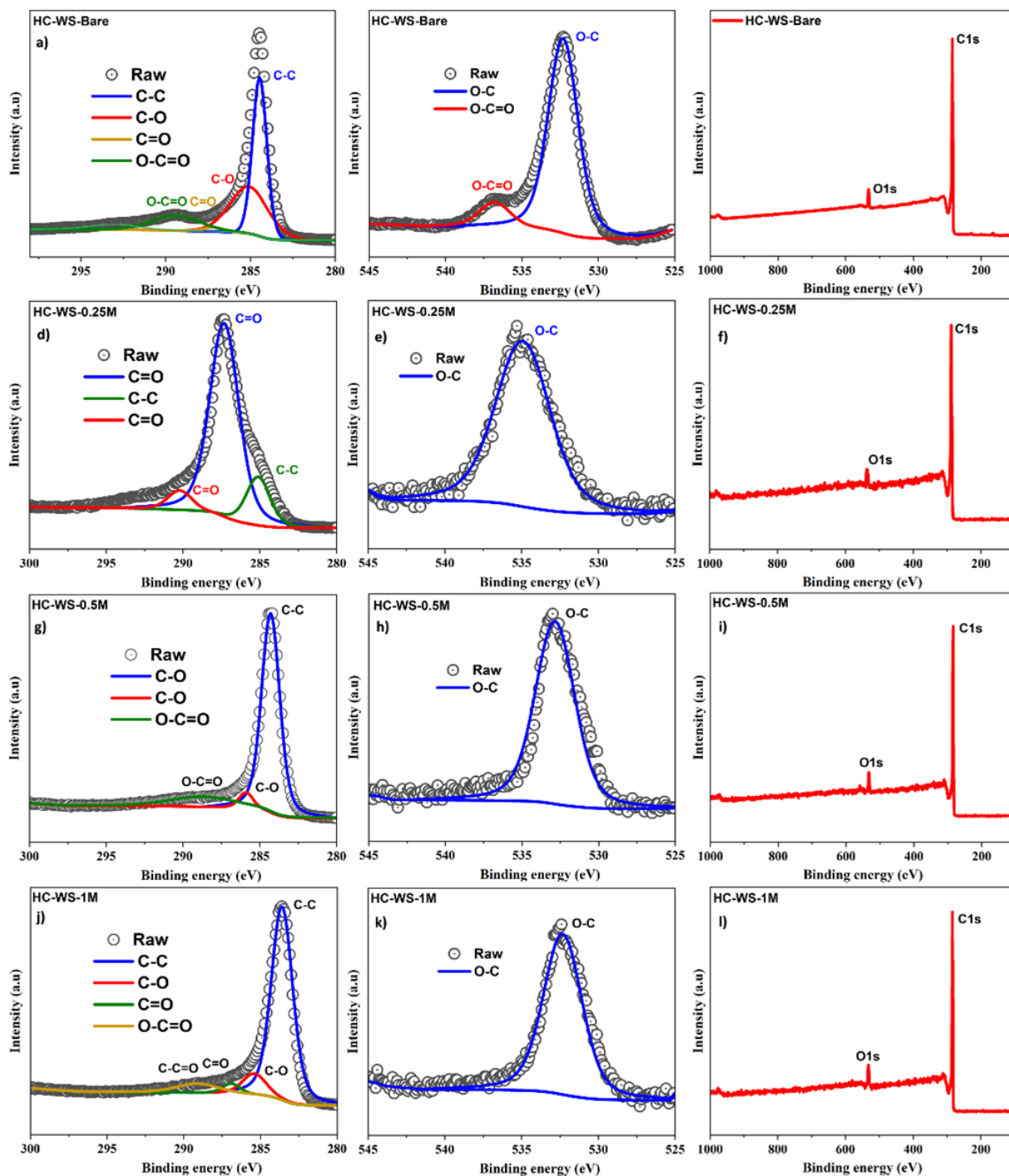


Figure 15. X-ray photoelectron spectroscopy (XPS) characterization of bare HC and sucrose-coated HC-S samples: high-resolution C1s spectra of (a) HC-WS-Bare, (d) HC-WS-0.25M, (g) HC-WS-0.5M, and (j) HC-WS-1M; O1s spectra of (b) HC-WS-Bare, (e) HC-WS-0.25M, (h) HC-WS-0.5M, and (k) HC-WS-1M; and survey spectra of (c) HC-WS-Bare, (f) HC-WS-0.25M, (i) HC-WS-0.5M, and (l) HC-WS-1M.

4.9 SEM-EDS analysis of surface morphology and elemental distribution

To further investigate surface morphology and elemental distribution at the electrodes, we performed scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS) (Fig. 16). The SEM images revealed significant morphological differences between the uncoated and sucrose-coated samples. The surface texture of uncoated HC-WS (Fig. 16a) was extremely irregular and rough, with prominent cracks and sharp edges, reflecting the inherent structural heterogeneity of biomass-derived carbon. The surface morphology gradually became smoother with increasing sucrose concentration. The surface features of the HC-0.25M sample (Fig. 16f) were smooth, while the HC-0.5M sample (Fig. 16k) exhibited a more uniform and continuous surface. In contrast, the HC-1M sample (Fig. 16p) appeared more compact, consistent with the formation of a thicker carbon layer and the onset of partial particle aggregation. Corresponding elemental distribution maps from energy-dispersive X-ray spectroscopy (EDX) provided further information on the spatial distribution of carbon and oxygen in the sample series. The carbon distribution maps (Figures 16c, h, m, r) confirmed the presence of a continuous carbon matrix in all samples. However, the oxygen distribution maps (Figures 16d, i, n, s) show a significant and gradual decrease in oxygen signal intensity from pure HC to the sucrose-coated sample. Pure HC exhibits a relatively high and more uneven spatial oxygen distribution, while the coated sample shows a more uniform and attenuated oxygen signal, indicating a decrease in surface oxygen content. Quantitative EDX analysis (Figures 16e, j, o, t) further confirms this trend. Pure HC-WS contains approximately 95.5 wt% carbon and 4.5 wt% oxygen. Following sucrose treatment, the surface oxygen content gradually decreases, reaching approximately 3.5, 2.8, and 1.0 wt% for samples with concentrations of 0.25 M, 0.5 M, and 1 M, respectively, while the carbon content increases accordingly. This systematic decrease confirms that the sucrose-derived carbon coating effectively modifies the elemental composition of the surface by reducing the relative concentration of oxygen-containing compounds. These observations are consistent with X-ray photoelectron spectroscopy (XPS) results, which also show a decrease in the number of oxygen-containing functional groups on the surface after sucrose coating. The reduction in the number of oxygen-containing active groups and the gradual smoothing of the electrode surface lead to a decrease in chemical activity at the electrode-electrolyte interphase. This suppresses irreversible side reactions during the initial charge and discharge cycles, increasing the initial Coulombic efficiency and improving long-term electrochemical stability.

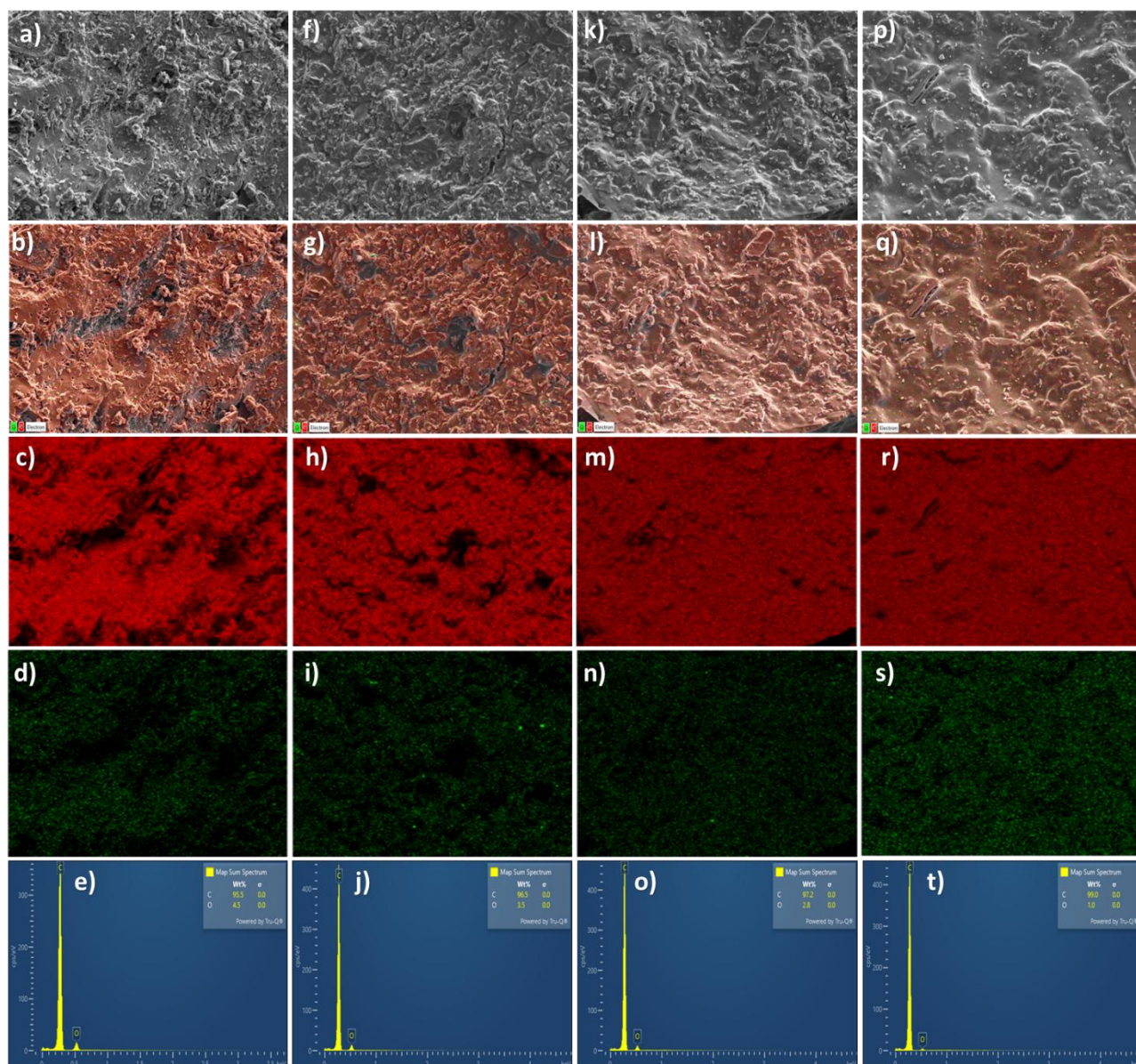


Figure 16. SEM morphology, elemental mapping, and EDS spectra of HC-WS and sucrose-impregnated samples: (a-e) bare HC-WS; (f-j) 0.25M sucrose-treated HC; (k-o) 0.5M sucrose-treated HC; and (p-t) 1M sucrose-treated HC.

Chapter 5. Conclusion

Hard walnut shell coal, a clean and widely available precursor derived from biomass waste, can be effectively modified using a sucrose impregnation strategy, making it suitable as an anode material for sodium-ion batteries. Unmodified hard walnut shell coal has a limited proportion of closed pores and a high density of surface defects, which together lead to low initial coulombic efficiency and significant irreversible sodium loss during the first charge-discharge cycle. By impregnating pre-carbonized walnut shell coal with sucrose solutions of varying concentrations, followed by controlled pyrolysis, a thin, amorphous layer of soft carbon can be formed on the particle surface, resulting in a composite co-carbon structure. This surface modification improves the material's surface structure and chemical composition by partially closing accessible open pores, reducing the concentration of oxygen-containing functional groups on the surface, and stabilizing the electrode-electrolyte interphase, thereby suppressing undesirable side reactions. Consequently, irreversible electrochemical processes are effectively suppressed, resulting in higher sodium ion storage efficiency and greater reversibility. Among all the samples studied, hard carbon treated with a 0.25 M sucrose solution demonstrated the most balanced electrochemical characteristics, with an initial coulombic efficiency of approximately 80%, and also showed stable long-term cycling performance and satisfactory rate characteristics. While higher sucrose concentrations (0.5 M and 1 M) can improve material performance, excessively thick coatings can limit Na^+ transport, potentially reducing overall electrochemical efficiency. In conclusion, this study demonstrates that proper sucrose impregnation is a simple, scalable, and cost-effective strategy for improving the electrochemical performance of sodium-ion battery anodes fabricated from biomass-derived solid carbon. The co-carbon strategy concept highlights the crucial role of controlled surface modification in regulating the porous structure and surface chemistry of solid carbon to improve sodium ion storage efficiency. Future research can explore alternative biomass precursors, different coating strategies, and combined surface modification methods to further optimize anode performance and extend this concept to other electrochemical energy storage systems.

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