

Sawdust-derived Hard Carbon as an Anode Material for Sodium-ion Batteries

M.Tech. Thesis

By

MEGHANA AGRAWAL



**DEPARTMENT OF METALLURGICAL ENGINEERING AND
MATERIALS SCIENCE**

INDIAN INSTITUTE OF TECHNOLOGY INDORE

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Sawdust-derived Hard Carbon as an Anode Material for Sodium-ion batteries

A THESIS

*Submitted in partial fulfillment of the
requirements for the award of the degree*

of

Master of Technology

By

MEGHANA AGRAWAL



**DEPARTMENT OF METALLURGICAL ENGINEERING AND
MATERIALS SCIENCE**

**INDIAN INSTITUTE OF TECHNOLOGY INDORE
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INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled "**Sawdust-derived Hard Carbon as an Anode Material for Sodium-ion Batteries**" in the partial fulfillment of the requirements for the award of the degree of **MASTER OF TECHNOLOGY** and submitted in the **DEPARTMENT OF METALLURGICAL ENGINEERING AND MATERIALS SCIENCE, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from June 2025 to May 2026. Thesis Submission under the supervision of Prof. Parasharam M. Shirage, Department of MEMS.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Meghana Agrawal

16-05-2026

Signature of the student with date

Meghana Agrawal

This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.


Dr. Parasharam M. Shirage
Professor
Department of Metallurgy Engineering
and Materials Science (MEMS)
Indian Institute of Technology Indore
Khandwa Road, Simrol,
INDORE-453552 INDIA

Prof. PARASHARAM M. SHIRAGE

Meghana Agrawal has successfully given her M.Tech. Oral Examination held on **11 May 2026**.


Dr. Parasharam M. Shirage
Professor
Department of Metallurgy Engineering
and Materials Science (MEMS)
Indian Institute of Technology Indore
Khandwa Road, Simrol,
INDORE-453552 INDIA

Signature of Supervisor(s) of M.Tech. thesis
Date:

Convener, DPGC

Date:

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Abstract

The increasing global energy demand and the environmental impact of fossil fuels have necessitated the development of sustainable energy storage systems. Among various alternatives, Sodium-ion batteries (SIB) have emerged as a promising technology for large-scale applications due to the natural abundance, low cost, and wide geographical availability of sodium resources. This research focuses on the synthesis and characterization of Hard Carbon (HC) derived from sawdust as a sustainable anode material for SIBs. The material synthesis involved a multi-step process, where sawdust was pre-treated with sodium hydroxide (NaOH) and hydrochloric acid (HCl), followed by hydrothermal treatment at 180 °C. The resulting precursor was carbonized at three different temperatures: 800 °C, 1000 °C, and 1200 °C to investigate the impact of thermal treatment on the structural and electrochemical properties. The HC 1000 sample demonstrated the best balance of performance, achieving a specific capacity of approximately 105 mAh/g at 0.05C and a superior capacity retention of 95% after 200 cycles at 0.2C. In contrast, HC1200 showed the highest long-term cyclic stability with an exceptional capacity retention of 99% over 200 cycles at 0.2C, although with a lower capacity. This work provides a sustainable pathway for utilizing biomass waste in high-performance energy storage applications.

Keywords: Carbonization, Intercalation, Sawdust-derived HC, Electrochemical performance

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Abbreviations

Sodium-ion batteries	SIB
Transition metal oxides	TMO
Hard carbon	HC
Standard hydrogen electrode	SHE
Solid electrolyte interface	SEI
Initial coulombic efficiency	ICE
Hydrothermal Carbonization	HTC
X-ray diffraction	XRD
X-ray photoelectron spectroscopy	XPS
Field emission scanning electron microscopy	FE-SEM
Transmission electron microscope	TEM
Brunauer-Emmett-Teller	BET
Galvanostatic charge-discharge	GCD
Cyclic Voltametry	CV
Ethylene Carbonate	EC
Diethyl carbonate	DEC
Intergovernmental panel on climate change	IPCC
Coulombic efficiency	CE

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Chapter 1

Introduction

1.1 Global Energy Demand

The rapid growth in global power consumption and the harmful environmental effects associated with conventional fossil fuels have intensified the need for sustainable energy technologies. Fossil-based resources, including coal, petroleum, and natural gas, release high levels of greenhouse gas emissions such as carbon dioxide (CO_2) and methane (CH_4), which are major contributors to climate change and global warming. Reports published by the IPCC emphasize that a significant reduction in fossil fuel usage is necessary to control the increase in global temperature and keep it below 2°C during this century. To address these environmental challenges, the United Nations has recognized affordable and clean energy as an important Sustainable Development Goal (SDG), promoting the adoption of cleaner and environmentally sustainable energy systems [1].

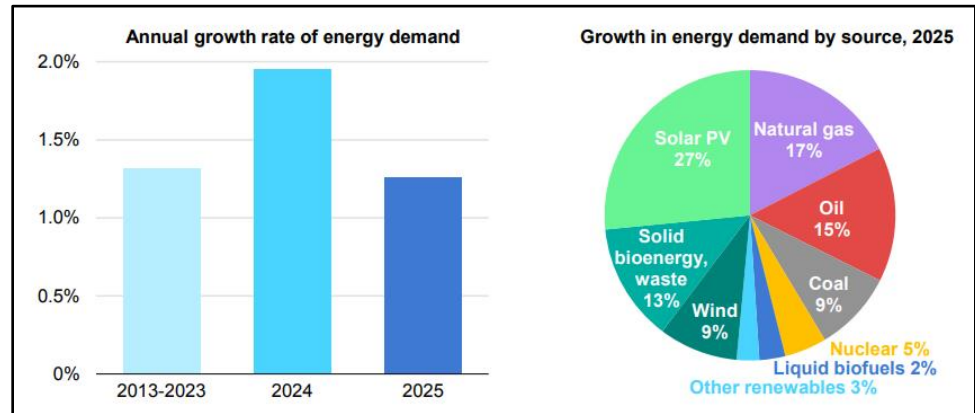


Fig. 1.1 Average annual growth in global energy consumption (2013–2025) and contribution of different energy sources in 2025 [2].

While renewable energy has high installed capacity, its actual electricity generation is low due to intermittency. This gap highlights the urgent need for energy storage systems, as shown in **Fig.1.1** Among various renewable energy options, solar photovoltaic and wind energy technologies have shown considerable potential for clean energy generation and have emerged as promising alternatives to conventional fossil-fuel-based energy generation. These energy sources are environmentally sustainable and widely available; however, they suffer from intermittent power generation because their output depends on environmental conditions such as sunlight and wind availability. Due to this variability, renewable energy systems cannot continuously provide electricity on demand, which limits their large-scale integration into the power grid. Therefore, efficient energy storage technologies are required to store abundant energy captured during peak production times and deliver it when energy demand increases.

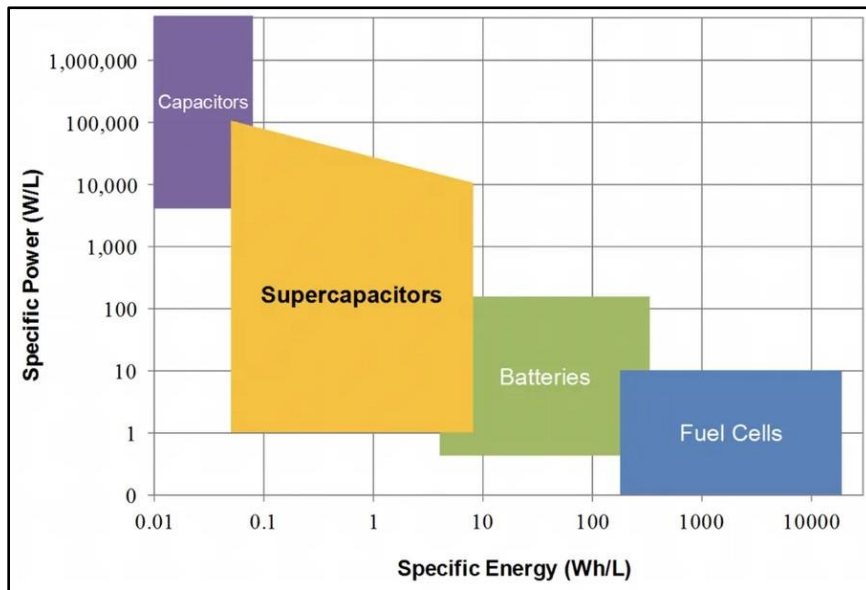


Fig. 1.2 Ragone plot comparing the specific power and energy density of various electrochemical energy storage systems [3].

While LIBs are the current industry standard, other technologies like fuel cells and flywheels offer alternative solutions for applications requiring either extreme energy storage or instantaneous power bursts. The Ragone plot, as shown in **Fig.1.2**, compares the energy and power density of various energy storage devices. Although batteries and supercapacitors are both used for energy storage, their operating characteristics are quite different, making them suitable for different applications. Two important parameters used to evaluate energy storage systems are energy density (Wh/L) and power density (W/L). Energy density refers to the quantity of energy that can be stored within a device, whereas power density indicates the rate at which the stored energy can be delivered. These characteristics play a crucial role in selecting an appropriate energy storage device for a specific application. Batteries generally possess high energy density but comparatively low power density, enabling them to store energy for longer durations. In contrast, supercapacitors exhibit very high power density with lower energy density, allowing rapid energy transfer. Therefore, while capacitors, supercapacitors, and batteries all function as energy storage devices, each serves a distinct purpose and cannot be directly substituted for one another.

Electrochemical energy storage systems, especially rechargeable batteries, have gained significant attention as an effective solution for integrating renewable energy into modern power systems. Among these technologies, Among the available battery technologies, LIBs are extensively utilized because of their high energy density, extended cycle life, and stable electrochemical performance. These batteries are extensively utilized in handheld technology electronic devices, sustainable transport, and utility-scale energy storage applications. For instance, grid-scale LIB installations have been implemented in several regions to support renewable energy infrastructure and improve power grid stability.

The Lithium triangle is geographically concentrated in the 'Lithium Triangle' (Chile, Argentina, and Bolivia), which holds over half of global resources, with production further centred in Australia and China [1].

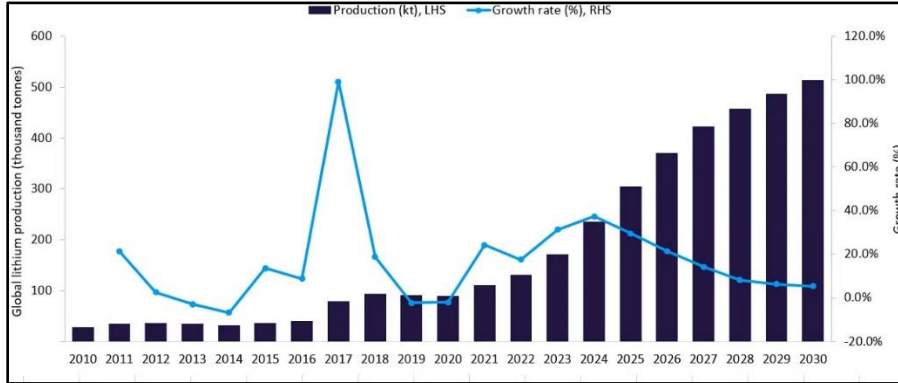


Fig. 1.3 Global Lithium Production and Growth Projections (2010–2030) [1].

As shown in **Fig. 1.3**, Global lithium production is projected to reach approximately 170.8 kilotons (kt) in 2023, representing a significant increase compared to 2022. This growth in lithium output is mainly driven by increased production activities in countries such as Australia and Argentina[4]. Global demand for rechargeable batteries has increased rapidly in recent years. The total battery demand was approximately 960 GWh during 2020-2021 and is expected to exceed 3200 GWh by 2030. Although LIBs dominate the current energy storage market, their large-scale deployment is limited by the uneven distribution and potential scarcity of lithium resources. Consequently, alternative battery technologies are being actively explored. Among various secondary battery systems, SIBs have emerged as a viable solution for large-scale energy storage. Commercial SIBs can deliver energy densities in the range of 100-160 Wh/Kg, which are comparable to those of LiFePO₄ batteries (150-200 Wh/kg) and significantly higher than other conventional storage systems such as Lead-acid batteries (30-40 Wh/kg), Ni-Cd/Ni-MH batteries (50-80 Wh/kg) and supercapacitors (5-10 Wh/kg). However, SIBs usually exhibit

lower energy density than LIBs because of their inherent material properties. particularly the larger atomic mass of sodium as compared to lithium. Despite being proposed earlier, SIBs received limited attention until around 2016, when increasing energy storage demands and fluctuations in lithium prices renewed interest in SIB technologies.

1.2 History of batteries

The development of batteries has evolved over several centuries as scientists sought reliable methods to store and supply electrical energy. One of the earliest known electrochemical devices is the Baghdad Battery, believed to date back to around **250 BC**, which consisted of a clay jar, an iron rod, and a copper cylinder and is often considered an early form of a galvanic cell.

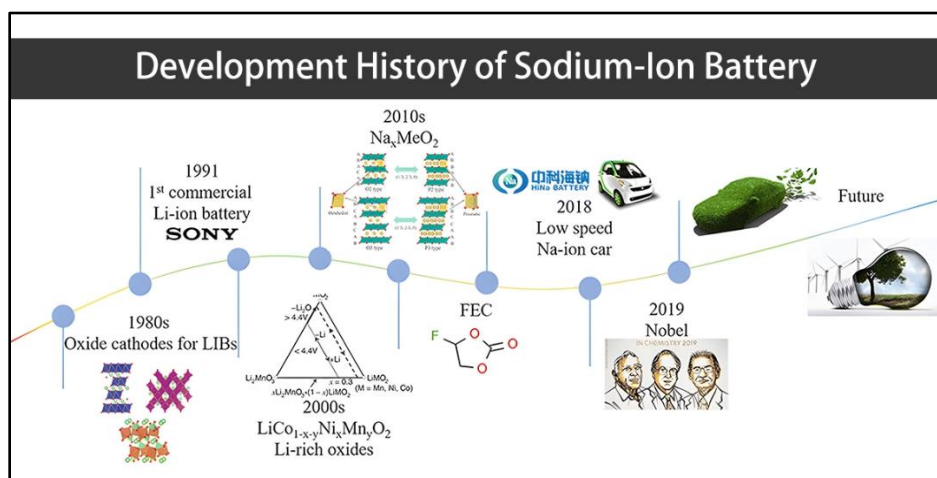


Fig. 1.4 History of battery innovations [5].

The lead–acid battery was first developed in 1859 by the French physicist Gaston Planté. It was one of the earliest practical rechargeable batteries and became widely adopted due to its ability to be reused after recharging. This feature provided a major technological advantage during that period. More than a century later, as shown in **Fig. 1.4**, Lithium-based batteries emerged as another major breakthrough in energy storage technology. Introduced in 1979, LIBs attracted substantial attention owing

to their high energy efficiency and lightweight nature. The major contributions of Stanley Whittingham, John Goodenough, and Akira Yoshino led to the development of modern lithium-ion batteries, for which they received the 2019 Nobel Prize in Chemistry. Today, LIBs are extensively employed in scooters, electric vehicles, industrial systems and many portable electronic devices. As a result, many technologies used in daily life depend on the energy supplied by these batteries. In 1980, John Goodenough introduced a cobalt oxide cathode material that significantly improved battery performance by increasing the operating voltage to nearly 4 V. This advancement enhanced the energy density while reducing the overall battery weight, making lithium batteries more suitable for advanced portable and transportation applications. The development was considered an important milestone for future electric mobility technologies.

Subsequently, in 1985, Akira Yoshino developed the first practical prototype of the LIBs. In this design, petroleum coke was used as the anode material in place of metallic lithium because it could reversibly accommodate lithium ions within its structure. This design allowed lithium ions to move repeatedly between the cathode and anode during charging and discharging without causing severe structural damage to the battery components. Consequently, the battery became lighter, exhibited high energy density, and could sustain hundreds of charge–discharge cycles. Yoshino patented this technology in 1985, and it was later commercialized by Sony in 1991, leading to large-scale production and major advancements in portable electronics and electric mobility systems.

1.3 Sodium-ion batteries

Sodium is abundantly available in the Earth's crust and is found in widely distributed natural resources across the globe, which provides a significant cost advantage for SIBs compared to LIBs. Because sodium resources are inexpensive and abundantly available, SIBs are considered suitable for large-scale energy storage systems, particularly for grid-level systems. They may also serve as potential alternatives for certain portable or disposable energy storage applications with further technological development. However, to achieve practical commercialization, SIBs still require improvements in several key performance parameters, including high energy density, excellent power capability, good coulombic efficiency, and stable long-term cycling performance. The performance parameters of Li-ion and Na-ion battery technologies are shown in **Table 1.1**. Consequently, extensive research efforts are currently focused on optimizing the main components of SIB, such as cathode materials, anode materials, electrolytes, and separators, in order to enhance their overall electrochemical performance [6]. Further research efforts in SIBs technology have particularly centred on the development of suitable anode materials. Among the various candidates, carbon-based materials are widely studied because of their abundant availability, chemical stability, and adaptable structural properties [6].

Table 1.1: Present performance parameters of Li-ion and Na-ion battery technologies [7].

Batteries	Gravimetric energy density (Wh/kg)	Volumetric energy density (kWh/m ³)	Life time (years)	Cycle life	Efficiency (%)	Working temperature (°C)
Li-ion battery	150-300	200-700	5-15	1000-12000	85-95	-20-60
Na-ion battery	90-160	250-375	10-15	500-8000	92	-40-80

SIBs operate on a similar electrochemical principle as LIBs, where ions move reversibly between the cathode and anode during charging and discharging. Because of this similar working mechanism, SIB technology can potentially utilize comparable materials and manufacturing processes. A major driving factor behind the development of SIBs is the replacement of lithium with sodium in the cathode and electrolyte components, along with the use of aluminum as the anode current collector instead of copper. In contrast to lithium, sodium does not form an alloy with aluminum, making aluminum a suitable and cost-effective current collector for SIB systems, which allows it to be used as a more economical current collector. In addition, sodium extraction from natural resources generally involves fewer environmental and economic challenges compared to lithium mining. SIBs are also considered relatively safer, as they are less prone to thermal runaway compared to many LIBs systems. However, sodium has a higher atomic mass than lithium, which results in lower theoretical energy density for SIBs. This limitation remains one of the main challenges and continues to motivate research focused on enhancing the electrochemical performance and cost effectiveness of SIBs technology [8].



Fig. 1.5 Schematic of a sodium-ion battery.

1.4 Why Sodium-ion batteries?

The development of electrochemical energy storage systems requires consideration of several key factors, such as cost per unit energy (kWh). Energy storage capability in terms of gravimetric (Wh/kg) and volumetric energy density (Wh/L), power density (w/kg), and the sustainability of the materials used. At present, LIBs dominate the global energy storage market due to their relatively competitive cost and high energy density. Current LIB technologies can achieve energy densities of approximately 260 Wh/kg, which is approaching their theoretical limit of around 300 Wh/kg. However, concerns have emerged regarding the long-term sustainability of LIB technology because lithium resources are relatively limited and unevenly distributed worldwide. In addition, the fast growth of electric vehicles (EVs) and the rising need for large-scale energy storage systems. Systems have significantly increased the consumption of lithium and cobalt, potentially leading to higher material costs in the future [9]. Furthermore, lithium and sodium ions differ considerably in their physical and chemical characteristics. Compared with lithium, sodium behaves as a weaker Lewis acid, leading to lower desolvation energy in several organic electrolyte systems. This characteristic can influence ion transport behaviour, particularly affecting ionic conductivity and interfacial charge transfer processes within the battery system.

1.5 Mechanism of the sodium-ion battery

SIBs are rechargeable energy-storage devices that operate by shuttling Na^+ between the electrodes during charging and discharging. They belong to the rocking-chair type battery system, similar to LIBs.

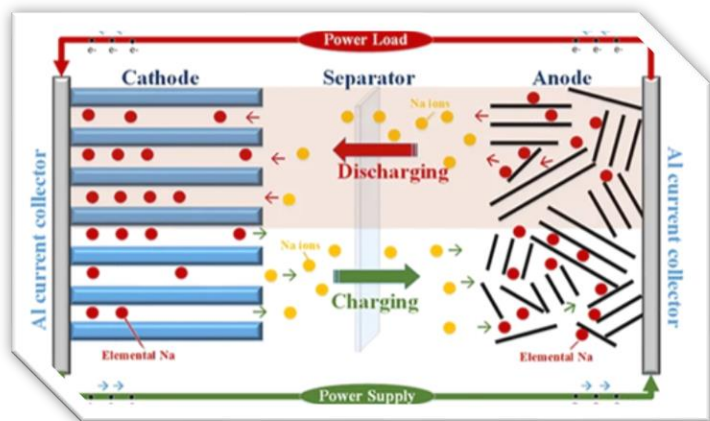


Fig. 1.6 Mechanism of a sodium-ion battery [10].

These electrochemical systems store electrical energy in chemical form and release it again as electrical energy when required. The operating mechanism of SIBs closely resembles that of LIBs and involves the reversible transport of Na^+ ions between two electrodes through an electrolyte medium. A typical SIB consists of a cathode and an anode separated by an electrolyte-filled separator. The electrolyte usually contains a sodium salt dissolved in a suitable solvent system, enabling sodium-ion conduction between the electrodes while preventing electron transport. In addition to providing sufficient ionic conductivity, the electrolyte should also support the formation of stable interfacial layers at the electrode-electrolyte interfaces. These interphases help prevent continuous decomposition of the electrolyte at high or low operating potential. Since the electrolyte interacts with various internal components of the battery, such as current collectors, separators, binders, and cell casing, it must be chemically and electrochemically compatible with all of them. This compatibility is essential to ensure long cycle life, stability, and safe battery operation. Commonly investigated cathode materials include sodium transition-metal oxides and Prussian blue analogues, whereas the anode is usually composed of disordered carbon materials, particularly HC, which can effectively store Na^+ insertion during battery operation.

During the initial charging process, electrical energy drives electrons from the cathode to the anode through the external circuit. At the same time, Na^+ are released from the cathode into the electrolyte to maintain charge balance and move through the electrolyte toward the anode, where they are inserted into the anode material. This process involves oxidation at the cathode and reduction at the anode, leading to an increase in the cell voltage. However, common electrolytes have a limited electrochemical stability window and may decompose at high potentials or low potentials. Hence, suitable anode and cathode pairs with optimum cutoff voltages are chosen. During the formation cycle, which is performed at very low C-rates (0.1C-0.05C), the electrolyte reacts with both electrodes and decomposes, forming an interfacial layer at the electrode-electrolyte layers namely the cathode-electrolyte interphase (CEI) on the cathode and the solid electrolyte interphase (SEI) on the anode. These interphases are essential for stable battery operation because they suppress continuous electrolyte decomposition. For effective performance, as shown in **Fig. 1.6**, as charging continues, sodium ions are extracted from the cathode and transported to the anode, where they are stored through adsorption and intercalation processes. Consequently, the cell voltage gradually rises until it reaches the preset charge cut-off voltage. During the discharge process, during discharge, both electrons and sodium ions move in the opposite direction, from the anode toward the cathode. Oxidation takes place at the anode, whereas reduction occurs at the cathode. As the electrochemical reactions continue, the cell voltage progressively drops until the cut-off voltage is reached.

In every charge-discharge cycle, sodium ions move between the two electrodes: from the positive electrode to the negative electrode during charging and back to the positive electrode during discharging. For a battery to achieve a long cycle life, it is essential that the sodium-ion storage processes remain highly reversible and that the electrolyte maintains good stability during repeated cycling [11].

Chapter 2

Anode materials for sodium-ion batteries

In rechargeable batteries, the electrode at which the oxidation reaction occurs during the discharge process is referred to as the anode. In SIBs, the anode acts as the negative electrode and serves as the host material for the reversible storage of sodium ions during electrochemical cycling. The selection of a suitable anode material is a critical factor influencing the electrochemical performance of SIBs. An ideal anode material should exhibit high reversible capacity, good electrical conductivity, structural stability during repeated charge-discharge cycles, and rapid sodium-ion diffusion kinetics. However, the development of high-performance anode materials for SIBs is more challenging than for LIBs. This challenge primarily arises from the larger ionic radius of sodium ions $\sim 1.02\text{\AA}$, which is significantly greater than that of lithium ions $\sim 0.76\text{\AA}$. The larger ionic size leads to slower diffusion kinetics and makes the insertion of sodium ions into many conventional electrode materials more difficult. As a result, several materials that perform well in LIBs show limited electrochemical performance when used in sodium-ion systems.

To address these limitations, various types of Anode materials have been explored for SIBs, as shown in **Fig. 2.1**. Based on the sodium storage mechanism, these materials are commonly divided into three major groups: intercalation-type, alloying-type, and conversion-type materials. Carbon-based materials such as graphite, soft carbon (SC), and hard carbon (HC) are widely investigated because of their good electrical conductivity, low cost, and stable structure. Among them, hard carbon has become one of the most suitable anode materials for sodium-ion batteries, because of its unique structural characteristics, such as disordered graphene layers, enlarged interlayer spacing, and the presence of micropores that can effectively accommodate sodium ions.

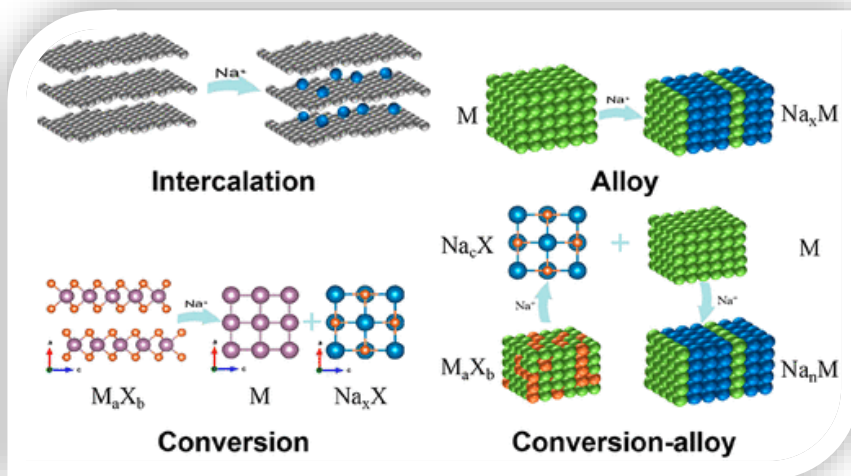


Fig. 2.1 Types of Anode material [12].

Insertion-type anode materials mainly include carbon-based materials and titanium-based compounds. These materials possess a stable host structure that allows the reversible insertion and removal of Na^+ ions during charging and discharging, without causing significant structural changes. However, graphite, which is widely used as an anode in LIBs, shows limited electrochemical activity in SIBs. This is mainly attributed to the incompatibility between its interlayer spacing and the larger ionic radius of Na^+ , which restricts efficient sodium intercalation.

In alloy-type anode materials, Na^+ react with metallic elements to form Na-metal alloys during the sodiation process. Typical alloying materials include tin (Sn), antimony (Sb), and phosphorus (P). These materials usually exhibit high theoretical capacities due to the formation of multiple sodium-rich phases. However, the alloying reaction is generally accompanied by large volume expansion, which can lead to mechanical stress and capacity degradation during repeated cycling.

Conversion-type materials store through Na^+ reversible redox reactions that convert metal compounds into metallic nanoparticles and sodium compounds. Transition-metal oxides, sulfides, and phosphides are

common examples of this class of materials. During the sodiation process, the metal compound reacts with Na^+ to form metallic particles and Na-containing phases, while the reverse reaction occurs during desodiation. Among these, intercalation-type materials such as HC are considered most suitable due to their superior structural stability and cycling performance.

2.1. Intercalation Type Anode Materials

Intercalation-type anode materials accommodate sodium through a reversible insertion mechanism in which Na^+ are accommodated within the host structure without causing significant structural changes. In this process, Na^+ ions are inserted into the interlayer spaces, channels, or vacant sites of the electrode material during charging and are extracted during discharge. Since the host framework remains largely intact during repeated sodiation and desodiation cycles, intercalation-type materials generally exhibit good structural stability and excellent cycle life. However, the intercalation of Na^+ is more challenging compared to Li^+ due to the relatively larger ionic size of Na^+ (1.02 Å). The larger size of Na^+ limits its ability to diffuse into materials with small interlayer spacing, thereby restricting the number of suitable host materials. As a result, many conventional intercalation materials used in LIBs, such as graphite, show poor sodium storage performance. Hence, the development of suitable intercalation-type anode materials with larger interlayer spacing and open structures is essential for efficient sodium storage.

Carbon-based materials are the most widely investigated intercalation-type anodes for SIBs. These include graphite, SC, and HC. Among them, graphite exhibits very limited sodium storage due to its small interlayer spacing (~0.335 nm), which is insufficient to accommodate sodium ions effectively. In contrast, disordered carbon materials such as SC and HC possess enlarged interlayer spacing and structural defects that facilitate sodium insertion.

Among intercalation-type materials, hard carbon has become one of the most suitable anode candidates for sodium-ion batteries. It consists of randomly oriented graphene layers with a turbostratic structure and contains abundant micropores and defects. These features provide multiple sodium storage sites, including interlayer spaces, surface defects, and nanopores. As a result, HC delivers comparatively high reversible capacity, stable cycling behaviour, and better sodium-storage characteristics than many other carbon materials. Apart from carbon-based materials, some titanium-based compounds, such as $\text{Na}_2\text{Ti}_3\text{O}_7$, have also been studied as intercalation-type anodes due to their stable framework and suitable sodium diffusion pathways. However, their relatively low electronic conductivity and limited capacity restrict their practical application. Overall, intercalation-type anode materials are considered advantageous for SIBs due to their structural stability and long cycle life. Among these materials, HC has attracted significant attention and is considered one of the most suitable materials for practical SIB applications. Therefore, in the present work, HC is selected as the anode material, and its structure, sodium storage mechanism, and electrochemical performance are discussed in detail in the following sections.

2.2 Carbon-based anode materials

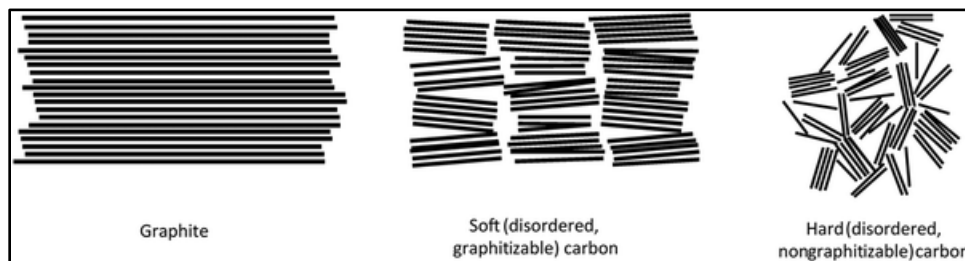


Fig. 2.2 Scheme illustrating the microstructures of graphite, SC and HC [13].

The comparison of structural morphology of carbon material describes the highly ordered layers in graphite, partially disordered layers in SC, and the random, non-graphitizable orientation in HC, as shown in **Fig.2.2**. The disordered structure of HC provides larger interlayer spacing and nanopores, making it the ideal host for sodium-ion intercalation.

2.2.1 Graphite

Graphite is the widely used anode material in LIBs, where it delivers a high theoretical capacity of about 372 mAh/g due to its well-defined layered structure. However, its performance in SIBs is significantly limited, especially in carbonate-based electrolytes, where the capacity drops to below 50 mAh/g. This limited performance mainly arises from the larger ionic size of sodium and the unstable nature of sodium-graphite intercalation compounds (Na-GICs), which restricts the effective insertion of Na^+ into graphite layers. Despite these limitations, graphite remains structurally stable and commercially viable, making it a potential candidate for SIBs if its limitations can be overcome. To improve its sodium storage capability, strategies such as increasing interlayer spacing through structural modification or introducing oxygen-containing functional groups have been explored. Another effective approach involves the co-intercalation of sodium ions along with solvent molecules, particularly in ether-based electrolytes, which facilitates reversible sodium insertion. These studies have improved the understanding of sodium storage behaviour in graphite and have also contributed to the development of graphite-based anode materials for SIBs provided insights into the storage mechanisms in HC materials [14].

2.2.2 Soft carbon

Amorphous carbon materials such as HC and soft carbon SC differ primarily in their graphitization behaviour at elevated pyrolysis temperatures. An increase in pyrolysis temperature promotes a higher

degree of graphitization and results in the development of a turbostratic disordered carbon structure. Compared to HC, SC generally forms comparatively larger and more ordered graphene layers along both the stacking direction and basal planes. In contrast, hard carbon HC is composed of small graphitic domains together with a large number of randomly distributed nanoscale pores, even after heat treatment above 2800 °C. Owing to its low cost, adjustable interlayer spacing, and good electrical conductivity, SC has attracted attention as a potential anode material for sodium-ion batteries. The presence of defects and porous structures in SC can contribute to high reversible capacity and favourable rate performance. For instance, SC prepared from suitable precursors has demonstrated capacities in the range of ~220–230 mAh/g with stable cycling behaviour. However, in practical full-cell configurations, SC often suffers from relatively low energy density, mainly due to its higher operating potential, which reduces the overall working voltage of the battery.

2.2.3 Hard Carbon

HC, commonly known as non-graphitizable carbon, is considered an important anode material for SIBs because of its distinctive disordered structure. The material mainly consists of curved and randomly arranged graphene layers with short-range structural ordering, along with a significant amount of nanopores formed between microcrystalline domains. Unlike graphitic carbon, HC does not transform into a well-ordered crystalline structure even at very high carbonization temperatures. Instead, its structure evolves with temperature, influencing key parameters such as the size of graphitic microdomains, the number of stacked layers, interlayer spacing, and pore distribution. These structural characteristics strongly influence sodium storage behaviour. The application of HC as an anode material was first systematically reported by Dahn and co-workers around 2000, where pyrolytic HC derived from glucose exhibited a high reversible capacity exceeding 300 mAh/g. Since then, HC has gained significant

attention and research interest, and a wide variety of precursors, including biomass, polymers, and organic compounds, have been explored to tailor its structure and electrochemical performance. The flexibility in precursor selection allows control over porosity, surface area, and defect density, which directly affect sodium storage mechanisms.

Substantial progress has been reported in recent years in improving the electrochemical performance of HC anodes. Strategies such as heteroatom doping (e.g., nitrogen doping), pore structure engineering, and morphology control have been employed to enhance conductivity and provide additional active sites for sodium storage. For example, nitrogen-doped HC derived from biomass sources has demonstrated improved energy density and cycling performance when paired with suitable cathode materials. Similarly, nanostructured and fibre-based HC materials have shown good capacity retention and stable long-term cycling behaviour.

Despite these advantages, HC still faces certain challenges, particularly related to initial irreversible capacity loss, moderate rate capability, and relatively limited cycling stability under high current densities. These issues are mainly associated with its complex pore structure and SEI formation. Therefore, ongoing research is focused on optimizing its microstructure and surface chemistry to overcome these limitations and further enhance its performance for practical SIBs applications [14].

2.3 Sodium storage mechanism in HC

Based on the early investigations of Stevens and Dahn (2000), the mechanism of SIBs in HC has remained a topic of continuous discussion. This is mainly because HC materials prepared from different precursors and synthesis conditions show significant variation in their structure and properties. In addition, it is difficult to accurately characterize features such as pore structure, defects, and microcrystalline regions, all of which strongly influence sodium storage behaviour during electrochemical

cycling. As a result, a single universal mechanism has not been fully established.

However, based on various experimental and theoretical studies, various models have been proposed to describe the sodium storage mechanism in HC. These include: (i) the intercalation–pore filling model, where sodium ions first intercalate between graphene layers and then fill nanopores; (ii) the adsorption–intercalation model, involving initial adsorption at defect sites followed by insertion into carbon layers; (iii) the adsorption–pore filling model, where sodium ions are stored through surface adsorption and pore filling; and (iv) a combined adsorption–intercalation–pore filling model, as shown in **Fig.2.3**, which considers all three processes contributing simultaneously to sodium storage [15].

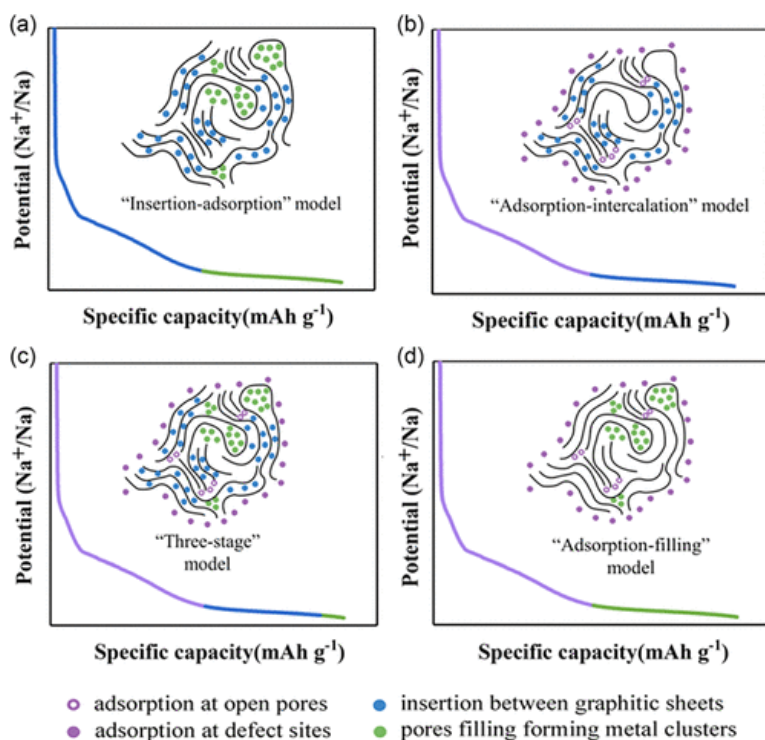


Fig. 2.3 (a-d) schematic of Na^+ storage mechanisms for HC [16].

2.3.1 Insertion-Adsorption

Sodium-ion storage begins with the adsorption of Na^+ ions onto defect sites, edges, and heteroatom-containing functional groups present in HC. These defect-rich regions provide energetically favourable sites for initial sodium uptake. As the sodiation process continues, Na^+ ions subsequently intercalate into the interlayer spaces of the disordered graphene structure. This mechanism is commonly observed in highly defective HC materials. In the voltage profile, the initial sloping region corresponds to adsorption, followed by a gradual transition toward intercalation at lower potentials.

2.3.2 Adsorption-pore filling

In the intercalation–pore filling mechanism, sodium storage initially takes place through the accommodation of Na^+ ions into the interlayer regions of HC. With a further decrease in potential, sodium ions start occupying the nanopores present in the carbon framework. These nanopores provide additional storage sites where sodium accumulates in the form of quasi-metallic clusters or fills the available pore volume. The low-voltage plateau observed in the charge–discharge curve is mainly related to this pore-filling process, whereas the sloping region is generally linked to ion intercalation. Using in situ XRD analysis, an increase in d-spacing was reported during the gradual sodiation of HC at voltages close to 0.1V. However, in situ XRD analysis of HC remains challenging because the disordered nature of hard carbon produces broad diffraction peaks and weak long-range structural order. Later investigations were unable to reproduce the same observations consistently.

2.3.3 Adsorption-intercalation pore filling

Recently, a combined model involving all three sodium-ion storage mechanisms has been introduced. According to this model, surface adsorption mainly contributes to sodium storage at potentials above 0.1 V.

At voltages below 0.1 V, sodium ions are first inserted into graphitic domains and subsequently stored within the pores of the hard carbon anode. This mechanism is commonly described as the adsorption–intercalation–pore filling model, is the most widely accepted and comprehensive model for sodium storage in HC. In this mechanism, Na⁺ ions are first stored at defect regions, edge sites, and surface functional groups, contributing to the sloping region at higher potentials. Subsequently, Na⁺ ions intercalate into the expanded and disordered graphene layers. Finally, at low potentials, sodium ions fill the nanopores and may form quasi-metallic clusters, leading to the characteristic low-voltage plateau. This multi-step mechanism effectively explains the combined slope and plateau behaviour observed in HC and is strongly dependent on structural features such as defect density, interlayer spacing, and pore distribution.

2.4 Research gap

(a) Unclear structure-performance Relation: The link between HC's microstructure (pores, defects, layers) and its electrochemical behaviour is not fully understood.

(b) Capacity Vs. Efficiency challenge: Optimisation attempts to increase specific capacity, often reducing the initial coulombic efficiency, making it difficult.

(c) Limited cycle stability: Significant capacity fading occurs during long-term charge-discharge cycling.

(d) Non-uniform production Quality: Biomass-derived HC shows batch-to-batch variations, and scalable, reproducible synthesis methods are still lacking.

2.5 Objective of this work

- To synthesize HC material from sustainable precursors using a controlled carbonization process at varying temperatures 800°C, 1000°C and 1200°C.
- To evaluate the impact of carbonization temperature on the structural morphology, crystallinity, and porosity of the synthesized anode materials.
- To evaluate the electrochemical performance capacity, rate capability and cycling stability of the HC anodes in sodium-ion battery half cells.
- To establish a correlation between the materials' structural properties and its sodium-ion storage mechanism to optimize the anode for high energy density applications.

Chapter-3

Physicochemical and Electrochemical Characterization

This chapter presents the physicochemical and electrochemical characterization of the prepared HC material to assess its potential as an anode for SIBs. Physicochemical characterization was performed to examine the structural, morphological, and textural features of the prepared material, as these properties strongly affect sodium storage performance. XRD analysis was used to study the crystal structure and interlayer spacing of the carbon material. Raman spectroscopy helped evaluate the degree of disorder and graphitic nature of the carbon framework. In addition, FE-SEM was used to observe the surface morphology and particle distribution, while BET analysis was conducted to measure the specific surface area and pore size distribution.

In addition to structural analysis, electrochemical characterisation plays an important role in understanding the sodium-ion storage mechanism and evaluating the performance of the material. (GCD) Measurements were performed to determine the specific capacity, Coulombic efficiency, and cycling stability. The combined analysis of physicochemical and electrochemical characteristics provides a clear understanding of the correlation between material structure and sodium storage performance. In particular, features such as enlarged interlayer spacing, defect density, and porous structure play a significant role in governing the adsorption, intercalation, and pore-filling mechanisms in HC. Therefore, this chapter focuses on correlating the structural characteristics of the material with its electrochemical behaviour to understand its overall performance.

3.1 X-ray diffraction

XRD is a commonly used analytical method for identifying crystalline phases and studying the structural properties of materials. It also provides information related to lattice parameters and interlayer spacing. For XRD analysis, the sample is generally converted into fine powder so that the average structural characteristics of the bulk material can be examined.

X-rays are electromagnetic waves with wavelengths typically ranging from about 0.1Å to 10Å. Because of their short wavelength and high energy, X-rays possess greater penetrating ability than ultraviolet, visible, infrared, or radio waves. The relationship between energy, frequency, and wavelength is expressed by the de Broglie relation.

$$E = h\nu = \frac{hc}{\lambda} \quad (3.1)$$

Where ν represents frequency, h is Planck's constant, c is the speed of light, and λ denotes the wavelength of the radiation [17]. As shown in **Fig. 3.1**, X-rays are produced when energetic electrons collide with a metal target within an X-ray tube. The tube generally contains a heated tungsten filament that acts as the electron source and a metal target, commonly copper, which serves as the anode. Heating the tungsten filament causes the emission of electrons, which are then accelerated toward the positively charged target under a high applied voltage.

When these energetic electrons strike the target atoms, inner-shell electrons are ejected, creating vacant positions in the lower energy shells. Electrons from higher energy levels then occupy these vacant states, releasing excess energy during the transition, which appears in the form of X-rays.

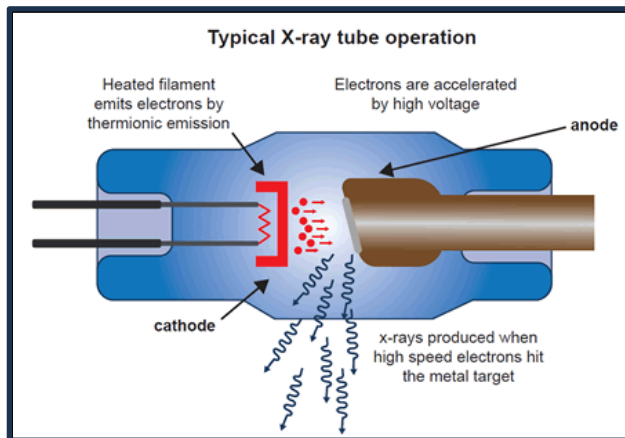


Fig. 3.1 Schematic of the X-ray generation tube [18].

These emitted X-rays have specific energies (or wavelengths) that depend on the type of target material and are called **characteristic X-rays**, as shown in **Fig.3.2**. For example, copper produces Cu K_α and Cu K_β radiations with fixed wavelengths. In addition to this, A portion of the X-rays is also generated when fast-moving electrons lose energy while passing close to the nucleus. This generates a continuous spectrum called **Bremsstrahlung radiation**, which has lower intensity and covers a wide energy range.

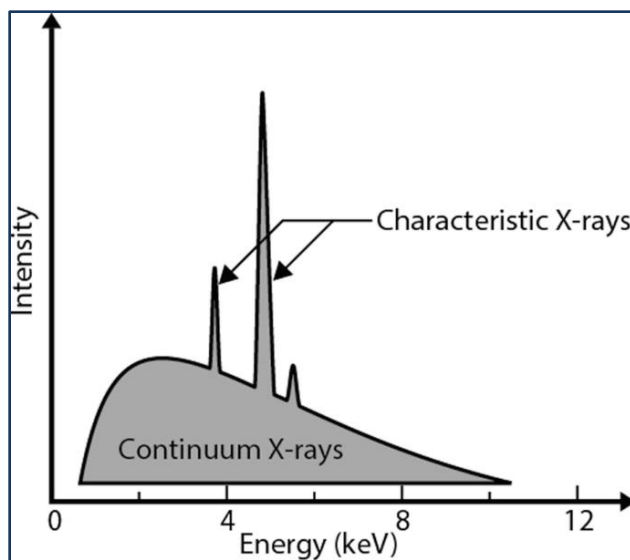


Fig. 3.2 Characteristic peaks of X-ray [19].

In 1912, Max von Laue demonstrated that crystals are capable of diffracting X-rays. because their atomic arrangement acts like a three-dimensional grating. XRD is commonly employed to analyze crystal structures and determine the spacing between crystallographic planes. XRD works on the principle of constructive interference produced when monochromatic X-rays interact with a crystalline material. In this technique, X-rays generated from an X-ray source are crystalline material. In this technique, X-ray sources are filtered to obtain a specific wavelength and then directed toward the sample surface. The detector records the diffracted beams for further analysis. As the diffraction angle (2θ) changes, different crystallographic planes meet the diffraction condition because the crystals in the powdered sample are randomly oriented, enabling detailed structural examination of the material.

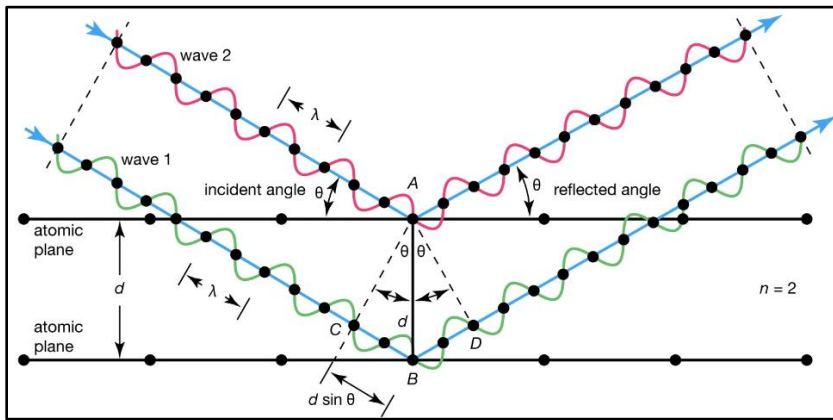


Fig. 3.3 Schematic of Bragg's law [20].

Bragg's law defines the condition under which constructive interference takes place for X-rays diffracted by parallel crystal planes. When monochromatic X-rays are incident on a crystalline material, they are diffracted from different lattice planes at specific angles. Since the reflected waves travel unequal distances, constructive interference is observed only

when the path difference corresponds to an integral multiple of the X-ray wavelength. This condition is mathematically expressed as:

$$n\lambda = 2d \sin(\theta) \quad (3.2)$$

where n indicates the order of diffraction, λ corresponds to the wavelength of the incident X-rays, d refers to the distance between neighbouring crystal planes, and θ represents the angle of incidence. Bragg's law forms the basis of XRD analysis, as shown in **Fig. 3.3** and is extensively used to evaluate interplanar spacing and investigate the crystal structure of materials.

3.2. X-Ray photoelectron spectroscopy

XPS is a surface-sensitive analytical method based on the photoelectric effect and is widely employed to examine the elemental composition and chemical states of materials. In this technique, the sample surface is exposed to monochromatic X-rays, typically Al K α or Mg K α radiation, which transfers energy to the atoms and causes the emission of core-level electrons. The kinetic energy of the emitted electrons is measured, and the binding energy is then calculated using the following equation:

$$BE = h\nu - KE - \phi \quad (3.3)$$

Where $h\nu$ represents the energy of the incident X-rays, kinetic energy is the measured kinetic energy of the emitted electrons, and corresponds to the work function of the instrument. As an energy element possesses a unique binding energy value, XPS can be used for elemental identification. present as well as their chemical bonding environment. The technique is highly surface-sensitive, typically analysing a depth of about 5–10 nm. The results are presented as a spectrum of intensity versus binding energy, where peak positions indicate different elements and their chemical states, and peak areas provide information about their relative concentrations.

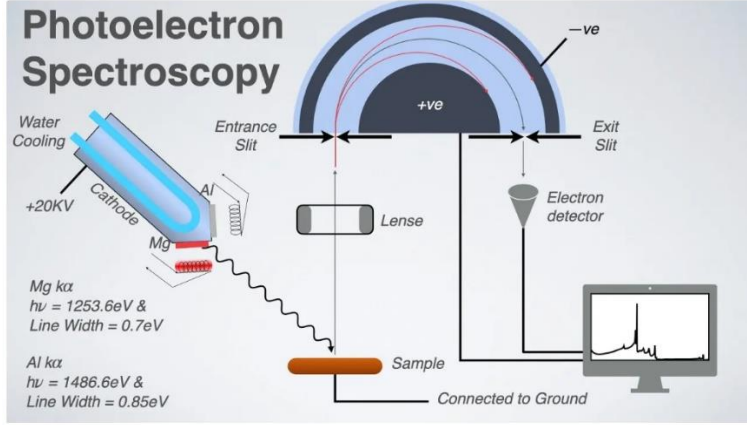


Fig. 3.4 Schematic representation of XPS instrumentation and working principle [21].

The kinetic energy of the emitted electrons is given by the following expression:

$$E_{Kinetic} = E_{photon}(h\nu) - E_{binding} - \phi \quad (3.4)$$

Here, h is Planck's constant, $h\nu$ represents the energy of the incident photon, and E_{photon} corresponds to the energy of the incident X-ray radiation. $E_{binding}$ denotes the binding energy of the electron, while ϕ is the work function, which represents the minimum energy needed to remove an electron from the material. By measuring and knowing E_{photon} and ϕ , the binding energy $E_{binding}$ is calculated, revealing the energy required to eject electrons from specific atomic orbitals. This binding, p energy varies depending on the element, orbital (e.g. s, d) and chemical environment, producing a spectrum of binding energies versus photoelectron counts that serves as a fingerprint for elemental identification and chemical state analysis. XPS spectra are typically presented as plots of photoelectron intensity versus binding energy. The spectrum generally consists of three types of peaks superimposed on a background. The core-level photoemission peaks are the most important for elemental identification. Valence band peaks, which appear at lower binding energies, give insight into the electronic structure of the material. In addition, Auger peaks,

generated by X-ray-induced Auger emission, are useful for chemical state analysis. Each peak corresponds to electrons with a specific binding energy that is characteristic of a particular element.

An XPS spectrum typically consists of several key features that help in analyzing the elemental composition and chemical states. The most important are the photoelectron lines, which are characteristic peaks of each element and form the basis of qualitative analysis; the most intense and symmetric peak is considered the main peak. In addition, satellite peaks may appear due to the non-monochromatic nature of X-ray sources, resulting in minor extra peaks beside the main ones. Auger electron lines are also observed, originating from relaxation processes after core-level ionization, and are generally broader and independent of the incident photon energy. Another significant feature is spin-orbit splitting, where energy levels (except s-orbitals) split into two peaks due to spin-orbital interaction, with fixed intensity ratios for p, d, and f orbitals. The separation between these split peaks can provide information about the chemical state. Sometimes, extra peaks known as ghost peaks may appear due to impurities in the X-ray source.

3.3. Raman spectroscopy

Raman spectroscopy is a widely used analytical technique for studying molecular structure and is often employed together with infrared spectroscopy. This technique is based on the Raman effect, discovered in 1928 by the Indian physicist C. V. Raman. During this process, incident light interacts with the material, and the majority of the scattered radiation undergoes elastic scattering, known as Rayleigh scattering. without any change in wavelength, while a small portion experiences inelastic (Raman) scattering due to molecular vibrations, resulting in a shift in wavelength as shown in **Fig. 3.5**. Since Raman scattering is extremely weak compared to Rayleigh scattering, special care is taken to minimize the stronger Rayleigh signal in order to clearly detect the Raman spectrum [22].

Raman spectra are recorded by exposing the sample to a high-intensity laser source and examining the scattered radiation with a spectrometer. The difference in energy between the incident and scattered light is known as the Raman shift and originates from molecular vibrational modes. In a Raman analysis, the intensity of the scattered radiation is represented along the vertical axis, whereas the Raman shift is plotted on the horizontal axis in units of wavenumber (cm^{-1}).

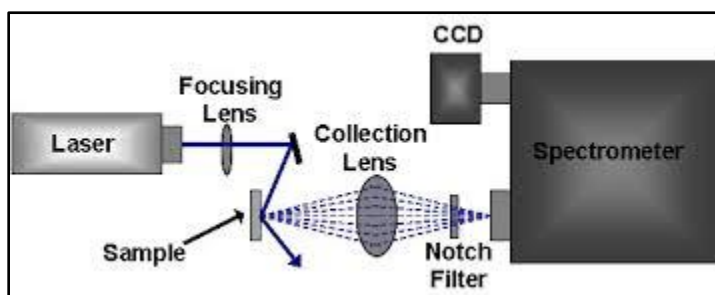


Fig. 3.5 Schematic representation of a typical Raman spectroscopy setup [23].

The Raman shift gives rise to two types of scattering signals. When the scattered radiation has lower energy and a longer wavelength than the incident light, it is referred to as Stokes scattering. In contrast, scattered light with higher energy and a shorter wavelength than the incident radiation is known as anti-Stokes scattering, as shown in **Fig. 3.6**. Raman spectroscopy is based on the inelastic scattering of monochromatic light, generally supplied by a laser source. During interaction with the material, most photons undergo elastic scattering without any frequency change, while a small fraction experiences inelastic scattering, resulting in a shift in frequency. Producing either an increase or a decrease in frequency relative to the incident radiation. This process is referred to as the Raman effect. The resulting frequency shifts provide information related to molecular vibrations, rotations and other low-frequency transitions. Owing to its effectiveness, Raman spectroscopy is extensively applied for the characterization of solid, liquid and gaseous materials. To better understand

Raman spectroscopy, it is important to distinguish between Rayleigh scattering and Raman scattering. Rayleigh scattering is the energy of the molecules that remains unchanged after interaction with the incident photons. Consequently, the scattered photons retain the same energy and wavelength as the incident photons. This process is elastic in nature, and no energy transfer occurs between the photon and the molecule.

During Raman scattering, incident light interacts with a molecule and causes distortion of its electron cloud through the oscillating electromagnetic field of the photon. This interaction briefly raises the molecule to an unstable virtual energy state. The molecule then relaxes to another energy level by emitting a scattered photon; the emitted light possesses a different frequency from that of the incident radiation. This change in energy characterizes the inelastic nature of Raman scattering.[24]

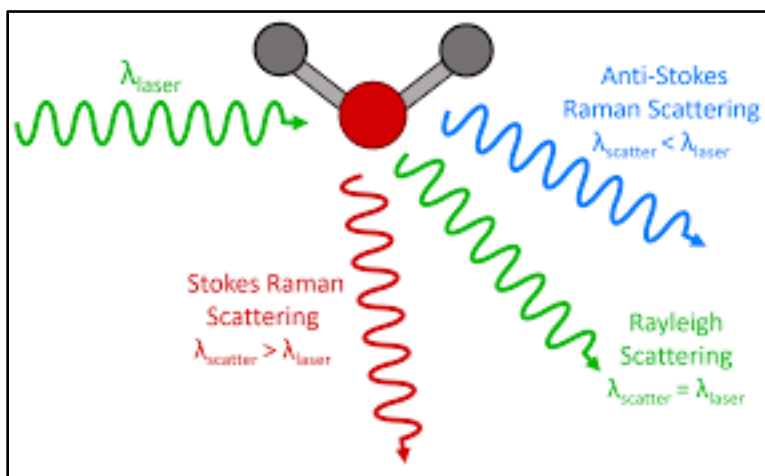


Fig. 3.6 Schematic representation of the Raman and Rayleigh scattering [25].

3.4. Field Emission Scanning Electron Microscopy

FE-SEM is a high-resolution characterization technique used to examine the surface features of materials by scanning them with a focused electron beam. The interaction between the electron beam and the atoms of the specimen generates different signals, which give information related to

surface morphology and elemental composition distribution. During analysis, the electron beam scans the sample in a raster pattern, and the detected signal intensity at each position is used to construct the image. In the most commonly used imaging mode, secondary electrons released from the sample surface are detected using an Everhart-Thornley detector. The intensity of these emitted electrons depends strongly on the surface morphology, which allows detailed observation of surface features and texture. Modern SEM instruments are capable of achieving spatial resolutions of less than 1 nanometer. In conventional SEM systems, specimens are typically examined under high vacuum conditions to ensure proper electron beam interaction and signal detection. However, advanced variants such as variable pressure or environmental SEM allow imaging under low vacuum or even in wet conditions. Additionally, specialized SEM instruments enable observations over a wide temperature range, including both cryogenic and elevated temperatures, depending on the experimental requirements.

In FE-SEM electrons are emitted from an electron source and accelerated through the microscope column using an applied voltage, generally in the range of 1-30 KeV. The electron beam is then refined and reduced in diameter using condenser lenses and apertures to obtain a fine and focused probe. The objective lens then concentrates the electron beam onto the surface of the sample, producing a spot size that can range from less than 1 nm to approximately 20 nm, depending on the operating conditions and instrument configuration, as shown in **Fig. 3.7**. The specimen is mounted on a stage inside the chamber, while the column and chamber are kept under vacuum, with spacing pumping systems to minimize electron scattering and obtain clear, high-resolution images. In some advanced SEM systems, variable pressure or low-vacuum modes are employed, allowing the sample chamber to operate at a lower vacuum level, which is particularly useful for imaging non-conductive or sensitive specimens.

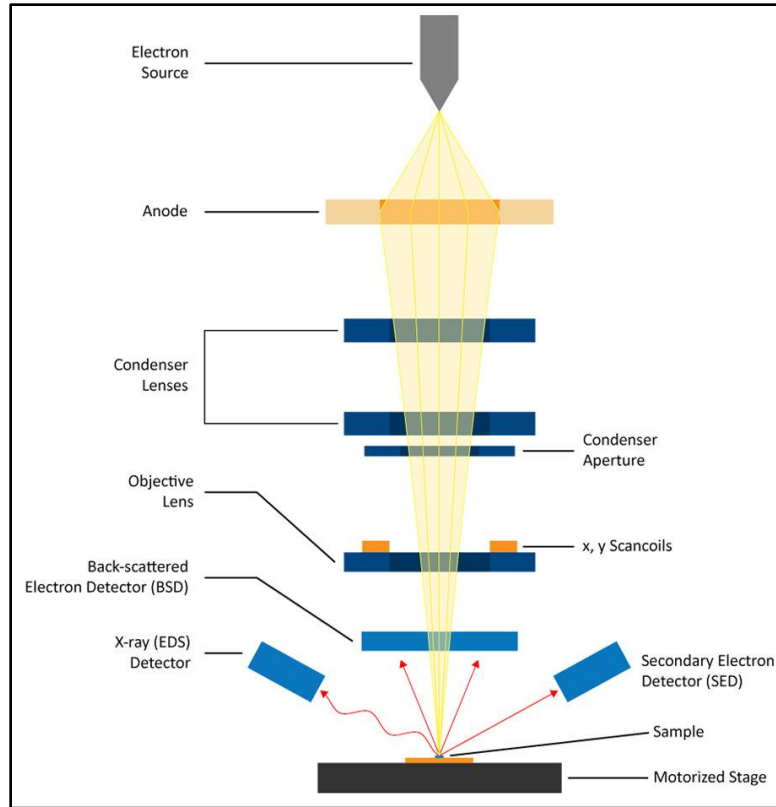


Fig. 3.7 Schematic of scanning electron microscopy [26].

When the electron beam comes into contact with the sample in SEM, it enters the material to a depth of several micrometres, forming an interaction volume where electron–atom interactions occur. The size and shape of this interaction volume depend on the accelerating voltage and the density of the sample. Higher accelerating voltage increases the penetration depth, while low-density materials produce an elongated tear-drop shaped interaction volume, whereas high-density materials result in a more hemispherical interaction volume due to increased scattering.

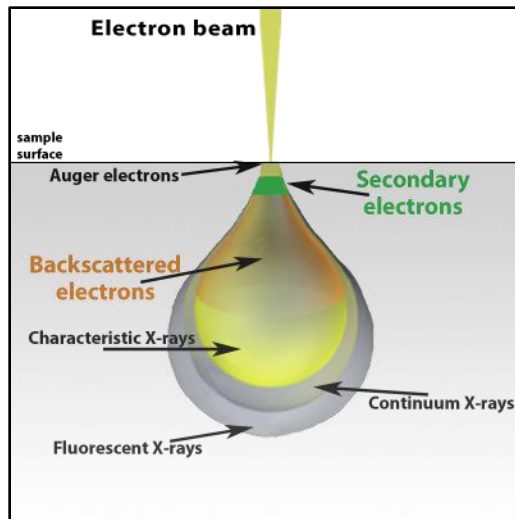


Fig. 3.8 Schematic of electron beam interaction [27].

The interaction of the electron beam with the sample generates different signals, among which secondary electrons, backscattered electrons, and characteristic X-rays are the most frequently utilized. As shown in **Fig. 3.8**, Secondary electrons, produced by inelastic scattering with energies below 50 eV, originate from near the surface and are primarily used for high-resolution topographical imaging due to their small interaction volume. Backscattered electrons, generated by elastic scattering at high angles, depend strongly on the atomic number of the material, with heavier elements producing a higher yield, thereby providing compositional contrast in images. Characteristic X-rays are generated when an ionized atom returns to a stable state as electrons transition between energy levels, and their energies are unique to each element, enabling precise elemental identification through techniques such as energy-dispersive spectroscopy (EDS). Additionally, a background X-ray signal is produced due to the deceleration of incident electrons. The overall resolution of SEM depends on factors such as the size of the electron beam and the interaction volume; however, atomic-level resolution cannot be obtained. Modern SEMs can reach resolutions below 1 nm.

3.5. Transmission electron microscopy

TEM is an advanced microscopy technique in which a focused electron beam is used to obtain highly magnified images with very fine structural detail. Unlike light microscopes, TEM can achieve magnifications of over two million times, allowing precise analysis of morphology, composition, and even crystallographic structure.

The development of electron microscopy was made possible after the discovery of the wave nature of electrons in the early 20th century, which enabled electrons to be manipulated similarly to light. Magnetic fields were then used as lenses to control and focus electron beams. Building on these principles, the first electron microscope was developed in 1931 by Ernst Ruska and Max Knoll, and later improved into the Transmission Electron Microscope in 1933 with industrial support. It offers significant advantages over optical microscopes due to its much higher resolution and magnification. It can resolve structures at the nanometer scale (around 0.2 nm), making it one of the most powerful tools available for material characterization and nanoscale analysis in modern laboratories [28].

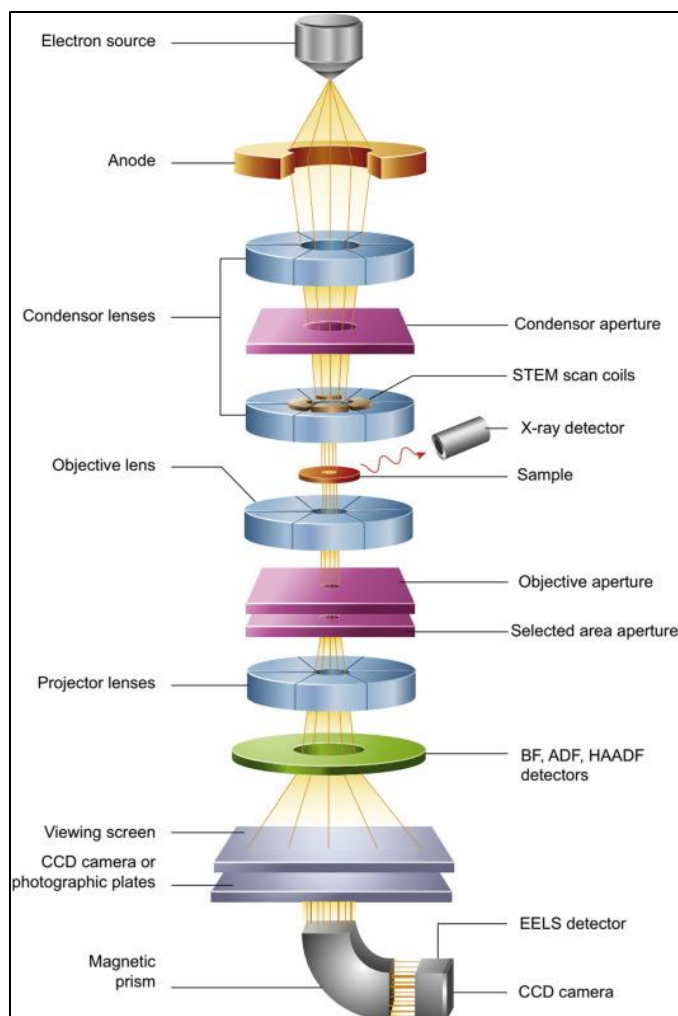


Fig. 3.9 Schematic of Transmission Electron Microscopy [29].

The operating principle of TEM involves the use of a high-energy electron beam for image formation rather than visible light. As shown in **Fig. 3.9**, electrons are generated from an electron gun and accelerated by applying a high voltage before interacting with the sample, which reduces their wavelength to the nanometer scale, thereby increasing the resolving power. The accelerated electrons are concentrated into a narrow beam with the help of electromagnetic lenses. This beam passes through an ultra-thin specimen, where the electrons interact with the material. Based on the structure and density of the sample, some electrons are transmitted while others undergo scattering. The transmitted electrons are then collected and

focused by objective, intermediate, and projector lenses to form a highly magnified image. Finally, the image is recorded on a fluorescent screen or digital detector. Because electrons possess an extremely short wavelength, TEM can achieve very high resolution and allows detailed examination of the internal structure of materials at the nanoscale.

3.6. Specific surface area and pore size analysis technique

BET theory explains the physical adsorption of gas molecules on solid surfaces and is widely applied for measuring the specific surface area of materials. It is based on multilayer adsorption using non-reactive gases, most commonly nitrogen at its boiling temperature. Other gases like argon, carbon dioxide, and water can also be used for analysis under different conditions. The measured surface area depends on the type of adsorbate and its properties.

The theory assumes that gas molecules form multilayers on the surface of the material, unlike the Langmuir theory, which considers only monolayer adsorption. In BET analysis, a non-reactive gas (adsorbate), most commonly nitrogen (N_2), is allowed to adsorb on the surface of a solid (adsorbent) at a constant temperature, usually 77 K. During the experiment, the quantity of adsorbed gas is determined at different relative pressures. Based on the BET equation, a plot is constructed to determine the amount of gas required to form a monolayer on the surface. From this monolayer capacity and the known cross-sectional area of the gas molecule, the specific surface area of the material is calculated. BET analysis is based on the physical adsorption of gas molecules on solid surfaces and is used to determine the specific surface area of materials. In this method, nitrogen is used as the adsorbate gas, while helium or hydrogen acts as the carrier gas. A mixture of these gases is passed over the sample at controlled relative pressures. At liquid nitrogen temperature (77 K), nitrogen molecules become physically adsorbed on the surface of the sample, whereas the carrier gas remains unabsorbed, resulting in an adsorption signal. Upon

removal of the liquid nitrogen, the temperature increases, and the adsorbed nitrogen is desorbed, producing a desorption signal. A known volume of pure nitrogen is then introduced for calibration to obtain a corrected peak. By varying the relative pressure through changes in the gas mixture composition, adsorption data at different pressures are obtained. These data are subsequently analyzed using the BET equation, which is used to calculate the monolayer adsorption capacity, which is further utilized to determine the specific surface area of the material [30].

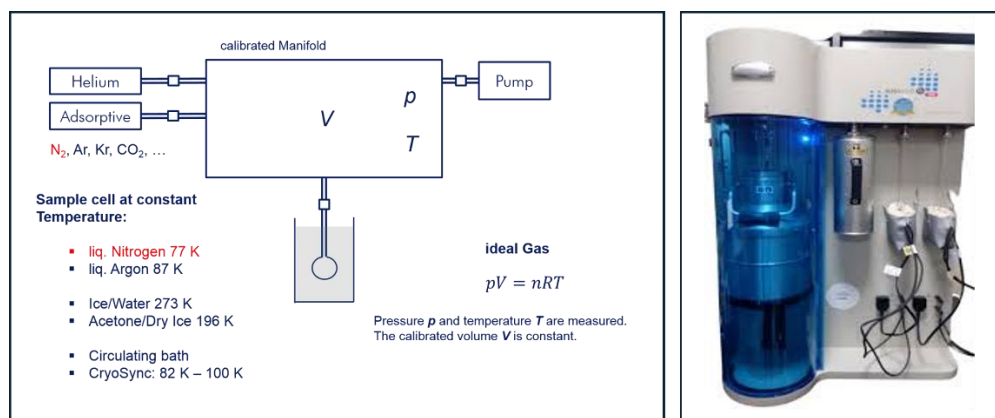


Fig. 3.10 Schematic of BET measurement setup [31].

Following the experimental setup shown in **Fig. 3.10**, adsorption data are collected at different relative pressures (P/P_0). The amount of nitrogen adsorbed on the material surface is measured at a constant temperature, and the obtained data are used to construct an adsorption isotherm. BET theory is applied to analyze the adsorption behaviour. The BET theory assumes multilayer adsorption on a homogeneous surface, where the first adsorbed layer has a distinct heat of adsorption, while the subsequent layers behave similarly to the condensation of gas molecules. It is further assumed that there is no interaction between the adsorbed layers.

The adsorption data in the relative pressure range of 0.05 to 0.3 are fitted using the BET equation, where v represents the volume of gas adsorbed at a given relative pressure (P/P_0), v_m corresponds to the

monolayer adsorption capacity, and c is the BET constant associated with the adsorption energy.

The BET equation is expressed in linear form by plotting $1 / [v((P_0/P) - 1)]$ vs (P/P_0) . The monolayer adsorption volume (v_m) is obtained from the slope and intercept of the linear BET plot. Using this value and the known cross-sectional area of a nitrogen molecule, the specific surface area of the material is calculated. The measured surface area depends on the quantity of gas needed to form a complete monolayer over the sample surface.

3.7. Galvanostatic charge-discharge curve

GCD is commonly used electrochemical technique for studying the performance of batteries and supercapacitors. In this technique, the device is charged and discharged under a constant current condition. current over a selected voltage window. GCD provides important information regarding specific capacitance, energy storage capability, and cyclic stability of the material. These techniques operate by a constant current to an electrochemical system during both charging and discharging within predetermined voltage limits. During the charging process, the potential of the electrode increases linearly with time, while during discharging, it decreases linearly under ideal conditions. In practice, deviations from linear behaviour are often observed due to internal resistance and electrochemical reactions. A sudden voltage drop at the transition from charging to discharging, known as the IR drop, arises due to the internal resistance of the system. Additionally, the presence of redox reactions leads to the formation of plateaus in the charge-discharge curves, indicating pseudocapacitive or battery-type behaviour.

In a typical three-electrode setup, A constant current is supplied to the working electrode, while the corresponding potential is recorded relative to a reference electrode. The magnitude of the applied current, commonly

represented as the C-rate, significantly influences the electrochemical performance of the system. Appropriate selection of the current and voltage window ensures accurate evaluation of capacitance and stability.

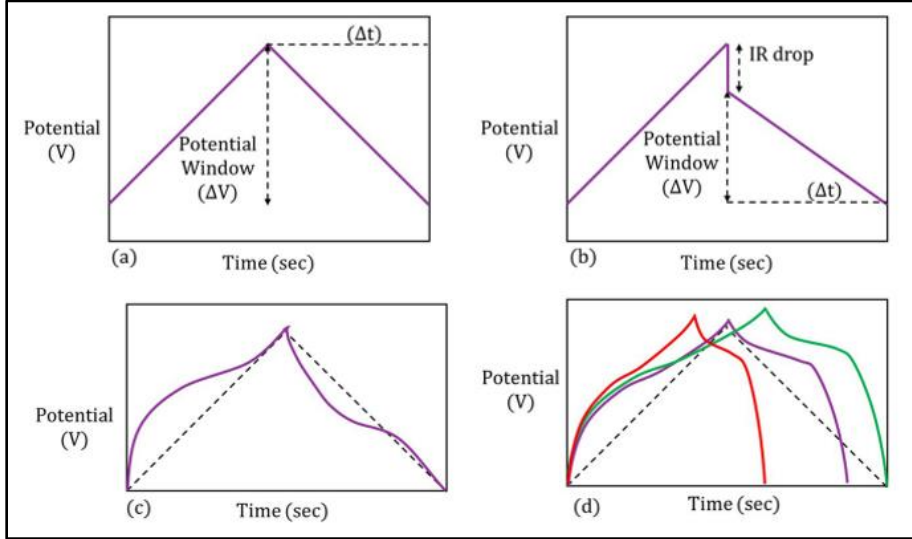


Fig. 3.11 GCD plot of (a) an ideal capacitor, (b) a real capacitor, (c) an EDL supercapacitor and (d) a pseudo-supercapacitor or battery [32].

The quantitative evaluation of electrochemical performance using the GCD technique is commonly carried out by calculating the specific capacitance (or specific capacity) from the discharge curve. The specific capacitance is determined using the slope of the discharge profile under constant current conditions.

The specific capacitance (C_s) can be calculated using the following relation:

$$C_s = \frac{I\Delta t}{m\Delta v} \quad (3.5)$$

where I is the applied current, Δt is the discharge time, m is the mass of the active material, and ΔV is the potential window excluding the IR drop.

In the case of battery-type materials, the specific capacity (Q) is often used instead of capacitance and is expressed as:

$$Q = \frac{I\Delta t}{m} \quad (3.6)$$

where Q is the specific capacity (in mAh/g), I is the applied current, Δt is the discharge time, and m is the mass of the active material. These parameters provide important insights into the charge storage capability of the material and are widely used to compare the electrochemical performance of different electrode materials.

3.8. Cyclic Voltammetry

Cyclic voltammetry (CV) is one of the most commonly employed electrochemical techniques for investigating the behaviour of energy storage systems. It involves monitoring the variation of current in response to a linearly changing applied potential over a defined voltage range. The typical experimental arrangement used for CV measurements. The two key parameters governing the CV measurement are the potential window and the scan rate. During the experiment, the applied potential is swept repeatedly between two preset limits. The speed at which the potential is varied is referred to as the scan rate, generally expressed in mV/s, while the selected range of potential is known as the operating potential window. One complete forward and reverse sweep constitutes a single cycle.

In a three-electrode configuration, the potential is applied between the working and reference electrodes, and the resulting current response is recorded. In a two-electrode system, the potential is applied across the device terminals. The measured current is plotted as a function of the applied potential to obtain a CV curve. For an ideal capacitive system, the current is directly proportional to the scan rate, which can be expressed as.

$$I = C \frac{dV}{dt} \quad (3.7)$$

where I represents the current, C is the capacitance, and dV/dt denotes the scan rate.

Chapter- 4

Experimental details and results

4.1. Material synthesis

Sawdust was used as the precursor for material synthesis. Initially, the raw sawdust was thoroughly washed with deionised (DI) water to remove surface impurities and subsequently dried. The cleaned biomass was then treated with NaOH to remove unwanted organic components. Thereafter, the sample was washed with 1M HCl to neutralize residual alkali and eliminate remaining impurities, followed by repeated washing with DI water until a neutral pH was achieved. The pre-treated material was subjected to hydrothermal treatment at 180°C. After hydrothermal processing, the obtained material was treated with sulfuric acid (H_2SO_4) and purified again using DI water until the pH became neutral, followed by drying. Finally, the dried material was subjected to pyrolysis in a tube furnace at various temperatures of 800 °C, 1000 °C, and 1300 °C to obtain carbonized materials with varied structural properties, as shown in **Fig. 4.1**, which were subsequently used for electrode preparation.

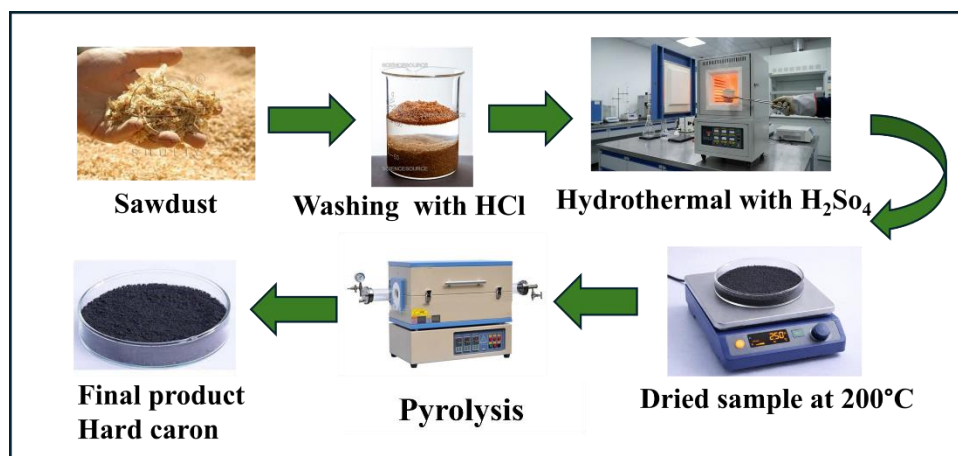


Fig. 4.1 Illustration of the preparation procedure for Sawdust-derived HC.

4.2. Electrode preparation

The synthesized carbon material was employed as the active material for electrode fabrication. The electrode slurry was prepared by mixing the active material with carbon black as the conductive additive and polyvinylidene fluoride (PVDF) as the binder in a suitable weight ratio, followed by the addition of N-methyl-2-pyrrolidone (NMP) to obtain a uniform mixture. The resulting slurry was coated uniformly onto a copper foil current collector using the doctor blade technique. The coated electrode was then dried under vacuum to remove the solvent and improve adhesion between the active layer and the current collector. After drying, the electrode was pressed to enhance mechanical stability and interfacial contact. Finally, the electrode was cut into appropriate dimensions and utilized for electrochemical characterization.

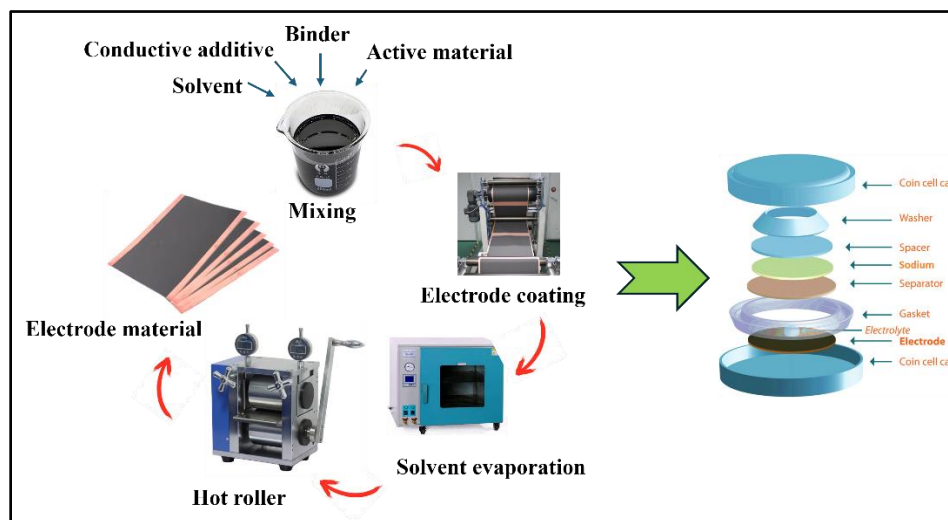


Fig. 4.2 Schematic of electrode preparation and coin cell fabrication.

To evaluate the electrochemical efficacy of the prepared HC, CR2032 coin-type cells were fabricated, as shown in **Fig. 4.2**. The assembly was carried out inside an ultra-pure Argon-filled glovebox, maintaining moisture and oxygen levels below 0.1 ppm. A half-cell configuration was employed, utilising metallic sodium as both the counter and reference

electrode. A [Glass Fibre] separator was utilized, thoroughly wetted with an electrolyte of [1 M NaPF₆ in EC/DEC (1:1 v/v)]. The sequential stacking of components from the negative casing to the spring was meticulously followed, and the cells were hermetically sealed using a hydraulic crimper at [800–1000 psi]. Post-fabrication, a 12-hour ageing period was provided to ensure optimal electrolyte penetration before initiating the tests.

4.3. Result and Discussion

To understand the performance of our sawdust-derived HC, it is important to look at both its physical structure and its behaviour in a battery. This chapter is divided into two parts to give a complete picture of the material. First, we discuss the morphology and structure of the carbon. Using tools like FE-SEM, TEM, XRD, Raman, XPS, and BET, we checked the shape of the particles, how the carbon layers are stacked, and the surface area. This helps us understand how the hydrothermal and heating processes changed the raw biomass into a functional material. After the structural study, we move to the electrochemical results. Here, we tested the material in coin cells using GCD to find the capacity and long-term cycling to check its cyclic stability. By analysing these results together, we can explain why this HC is a good candidate for SIBs.

4.3.1. XRD analysis

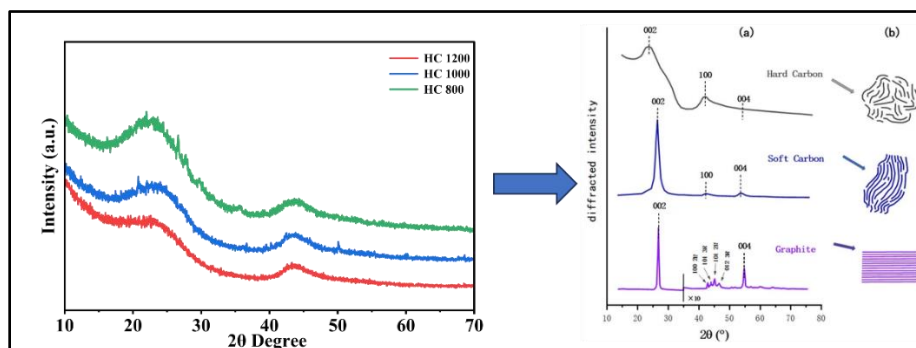


Fig. 4.3 a) XRD pattern of HC, b) Comparative XRD pattern of HC, SC, and graphite [33].

The structural characteristics and phase purity of the synthesised sawdust-derived HC were investigated using XRD. The XRD pattern shown in **Fig. 4.3** displays two broad diffraction peaks located around $2\theta = 24.1^\circ$ and 43.8° , which are indexed to the (002) and (100) planes of disordered carbon, respectively. The pronounced broadness of the (002) peak confirms the predominantly amorphous and turbostratic nature of the material, a typical characteristic of non-graphitizable HCs. The shift of the (002) peak towards a lower angle compared to pristine graphite 26.6° indicates an expanded interlayer spacing ($d_{(002)}$), calculated to be approximately 0.37-0.38 nm. This increased d-spacing is significantly larger than that of graphite (0.33nm). This enlarged interlayer spacing, compared to graphite (0.33 nm), facilitates the reversible insertion and extraction of relatively larger sodium ions (Na^+). Furthermore, the weak and broad (100) peak suggests a low degree of long-range graphitic ordering, which is beneficial for creating accessible nanopores for efficient sodium storage.

4.3.2. Raman spectroscopy

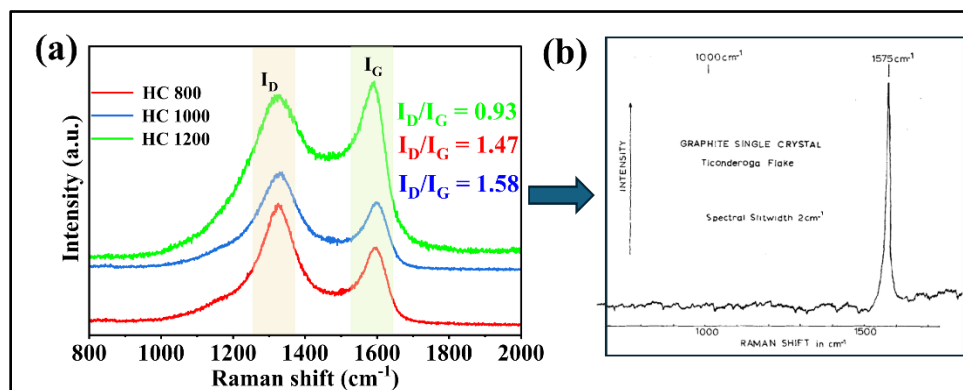


Fig. 4.4 (a) The Raman spectra of HC at different temperatures (800-1200°C), (b) Raman spectra of graphite [34].

The Raman spectrum of the sawdust-derived HC shows two prominent peaks, the D-band at 1350 cm^{-1} and the G-band at 1580 cm^{-1} . The high intensity of the D-band relative to the G-band indicates a significant concentration of structural defects and disordered sp^3 carbon sites, which is a hallmark of biomass-derived HCs. The calculated I_D/I_G ratio confirms the material's low degree of graphitisation and highly amorphous nature. These structural defects and disordered domains are essential as they offer accessible sites for sodium-ion storage and adsorption. As the temperature increases from 800°C to 1000°C , the I_D/I_G ratio increases from 1.47 to 1.58, indicating that the higher temperature initially promotes the formation of more structural defects and active edges within the carbon framework. These structural defects and disordered domains are essential as they provide more active sites for Sodium-ion adsorption, directly contributing to the enhanced electrochemical capacity of the HC 1000 anode. However, at 1200°C , the I_D/I_G ratio significantly decreases to 0.93, signifying a transition where further heat treatment reduces structural defects and promotes the growth and alignment of graphitic nanodomains. This lower ratio at 1200°C indicates improved structural order and densification, which reduces the number of available active sites for sodium storage, contributing

to the overall electrochemical capacity of the anode. An increase in temperature reduces structural defects and promotes the growth of graphitic nanodomains, resulting in a lower I_D/I_G ratio, indicating improved structural order.

4.3.3. FESEM analysis

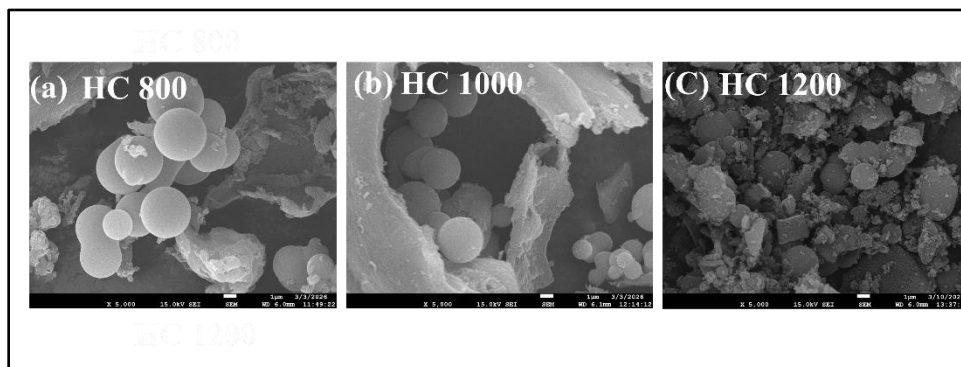


Fig. 4.5 FESEM images of (a) HC 800, (b) HC 1000, (c) HC 1200.

The surface morphology and structural transformation of sawdust-derived HC under different carbonisation temperatures (800, 1000, and 1200°C) as shown in **Fig. 4.5** were investigated via SEM. The material predominantly exhibits a discrete spherical morphology with smooth surfaces, which is a characteristic result of the hydrothermal pre-treatment. As the temperature increases to 1000°C, the spherical particles remain largely intact but undergo noticeable thermal contraction and densification, leading to a more robust and interconnected framework. This stability at 1000°C suggests an optimal balance between carbonisation and structural preservation. However, at 1200°C, a significant morphological transition is observed where the microspheres begin to fragment and fuse into irregular clusters. This degradation is attributed to the aggressive release of volatile species and the internal stress caused by high-temperature shrinkage. These findings indicate that the spherical architecture is best preserved at 1000°C, which facilitates ensuring uniform electrolyte accessibility and efficient sodium-ion diffusion pathways in battery applications.

4.3.4. BET analysis

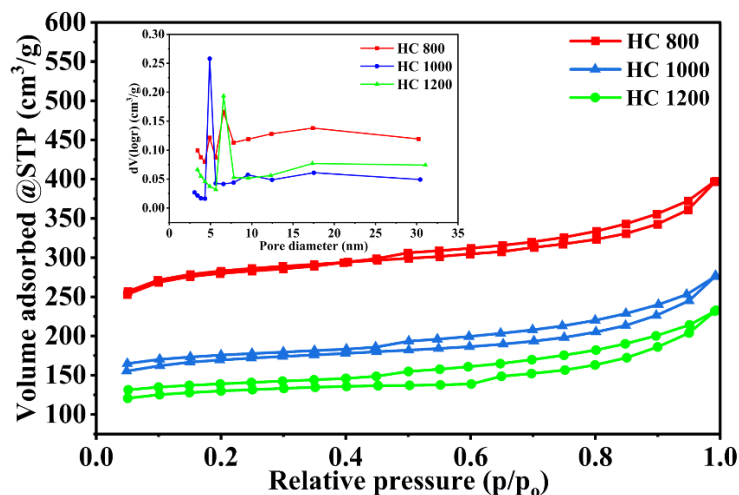


Fig. 4.6 N₂ adsorption/desorption isotherm and pore size distribution.

Table 4.1: Specific surface area and pore diameter of HC sample at different temperatures.

Temperature(°C)	Specific surface area (m ² /g)	Pore diameter (nm)
HC 800	721.024	6.43
HC 1000	349.319	5.63
HC 1200	295.021	6.54

The textural properties of the HC samples were investigated through N₂ adsorption-desorption measurements, and the results are shown in **Fig.4.6**. All samples exhibit Type-IV isotherms with an H3-type hysteresis loop, confirming a predominantly mesoporous structure. As the carbonisation temperature increases from 800 to 1200°C, the specific surface area (SSA) shows a sharp decline, which is primarily attributed to

the thermal densification and the closure of micropores at elevated temperatures. Conversely, the average pore diameter increases with temperature; this is due to the coalescence of smaller pores into larger ones under high thermal energy. Notably, HC 1000 demonstrates an optimised architecture with a balanced surface area and pore size, facilitating rapid Na-ion diffusion. For the HC 1200 sample, the desorption branch does not overlap with the adsorption branch at low relative pressures. This open-loop behaviour indicates the narrowing of pore entrances, leading to the trapping of nitrogen molecules within the carbon framework. These results suggest that 1000°C is the critical temperature for maintaining an ideal pore structure for efficient sodium storage.

4.3.5. HR-TEM analysis

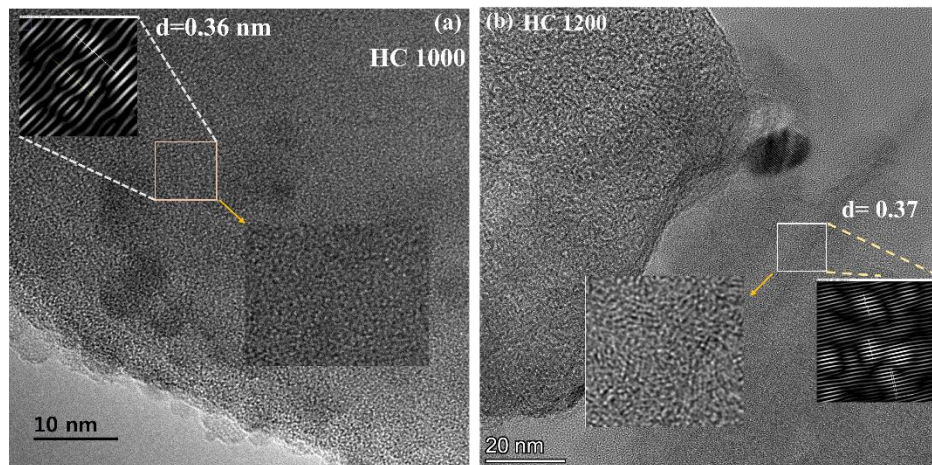


Fig. 4.7 (a,b) HRTEM image of HC at different temperatures.

The nanostructure and interlayer lattice spacing of the HC samples were further analyzed using HR-TEM. **Fig.4.7** reveals the typical turbostratic (disordered) structure of HC, characterised by short, randomly oriented graphene-like nanodomains. At 1000°C, the carbon layers are highly disordered with a relatively large interlayer spacing $d_{(002)}$ of approximately 0.375 nm, which is conducive to the intercalation of larger Sodium ions. However, as the temperature increases to 1200°C, the HR-

TEM images show a higher degree of structural orientation. The lattice fringes become more elongated and parallel, with the d-spacing decreasing to approximately 0.36nm. This reduction in d-spacing and the growth of graphitic domains confirm that higher carbonisation temperatures promote the partial graphitisation of the carbon framework. These observations are in perfect agreement with the XRD data, validating that HC1000 maintains a more expanded and disordered structure suitable for high-capacity sodium storage.

4.3.6. XPS analysis

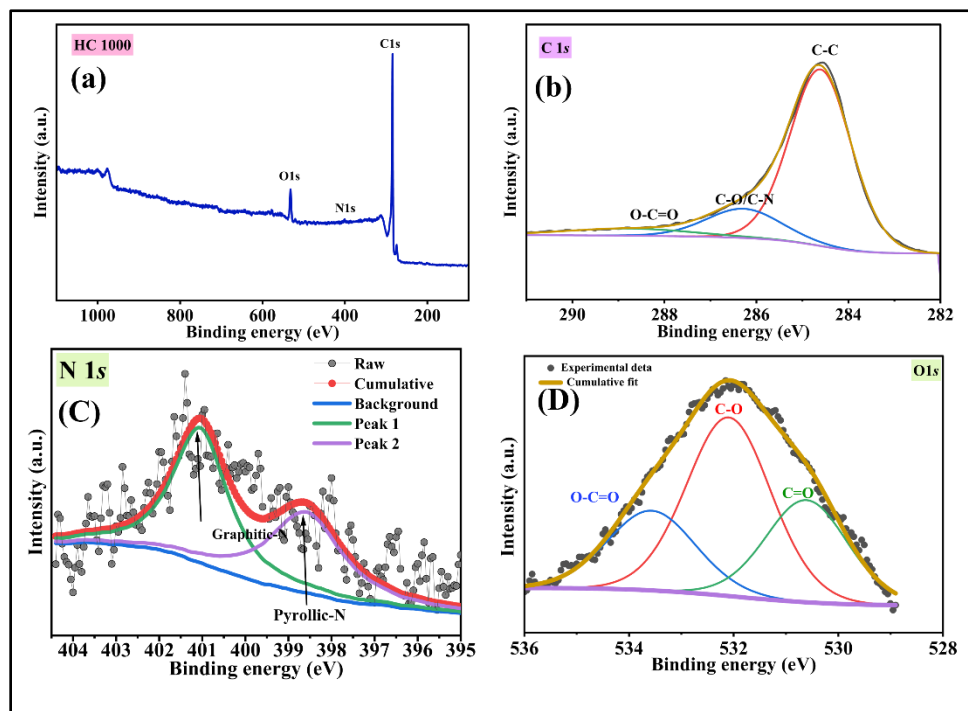


Fig. 4.8 (a) Survey spectra of HC, (b) Core level XPS spectra of C 1s, (c) O 1s, (d) N 1s

The surface elemental composition and chemical oxidation states of the HC 1000 sample were systematically investigated using XPS. As shown in survey spectra in **Fig. 4.8 (a)**, the presence of clear peaks for Carbon (C 1s), Oxygen (O 1s), and Nitrogen (N 1s) confirms the successful synthesis of heteroatom-doped HC derived from sawdust. To further understand the

chemical environment, high-resolution spectra were deconvoluted and analysed based on their specific binding energies. The C 1s spectrum **Fig. 4.8 (b)** is dominated by a sharp peak at 284.6 eV (72.07 at.%), assigned to the sp^2 -hybridized C-C/C=C bonds, which signifies a high degree of carbonisation. The additional peaks at 286.27 eV (C-O/C-N) and 288.76 eV (O-C=O) represent surface functional groups. The O 1s spectrum **Fig. 4.8 (c)** Further shows peaks at 532.09 eV (C-O) and 530.61 eV (C=O), which improve the surface wettability towards the electrolyte. Crucially, the N 1s spectrum **Fig. 4.8 (d)** reveals a distinct peak at a binding energy of 400.92 eV (1.19 at.%), which is primarily associated with Pyrrolic and Graphitic nitrogen species. These nitrogen dopants are essential as they introduce structural defects and active sites that enhance sodium-ion adsorption. Quantitatively, the atomic composition of 72.07% Carbon, 1.19% Nitrogen, and 6.77% Oxygen demonstrates a well-balanced heteroatom doping. This unique surface chemistry is highly favourable for achieving superior capacity and long-term stability in SIBs.

4.3.7. Galvanostatic charge-discharge curve

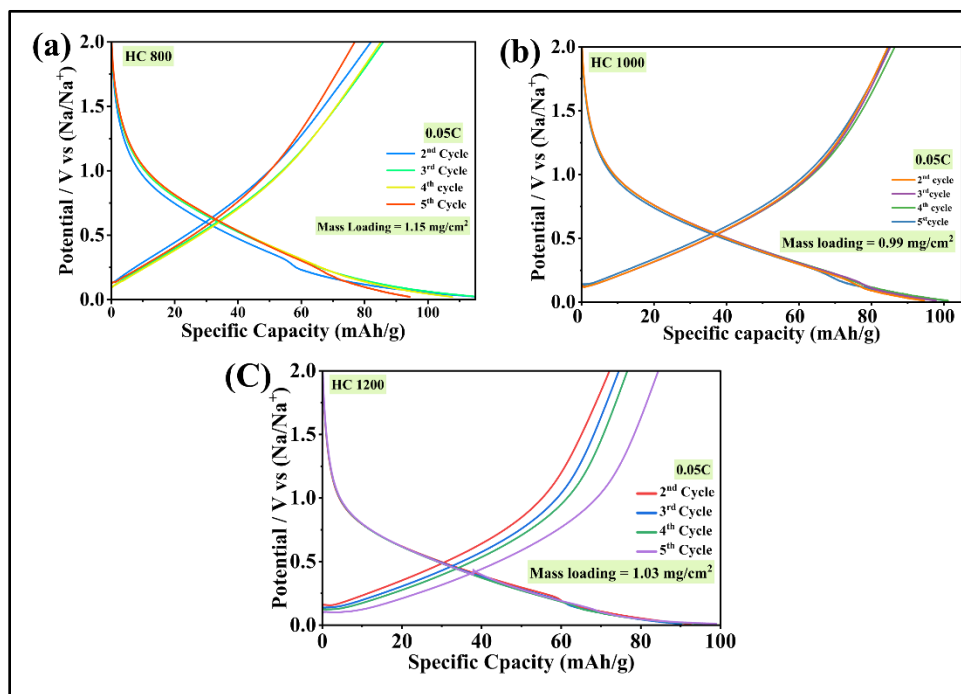


Fig. 4.9 GCD profile of (a) HC 800, (b) HC 1000, (c) HC 1200 at 0.05 C.

The electrochemical stability of the HC samples was evaluated using GCD profiles at 0.05 C as shown in **Fig.4.9** . A critical observation in the HC 1000 sample is the precise convergence of the charge and discharge curves at the same point, indicating superior Coulombic Efficiency compared to HC 800 and HC 1200. This behaviour signifies excellent electrochemical reversibility, where the structural framework at 1000 °C allows for the seamless insertion and extraction of Sodium ions without significant energy loss. While HC 800 shows slight deviations and HC 1200 suffers from reduced active pathways, HC 1000 maintains a stable 'Sloping-to-Plateau' transition. The near-perfect overlap of the 2nd to 5th cycles in HC 1000 further confirms that the material undergoes minimal structural strain during cycling, making it the most reliable architecture for long-term Sodium-ion storage.

4.3.8. Galvanostatic charge-discharge curve

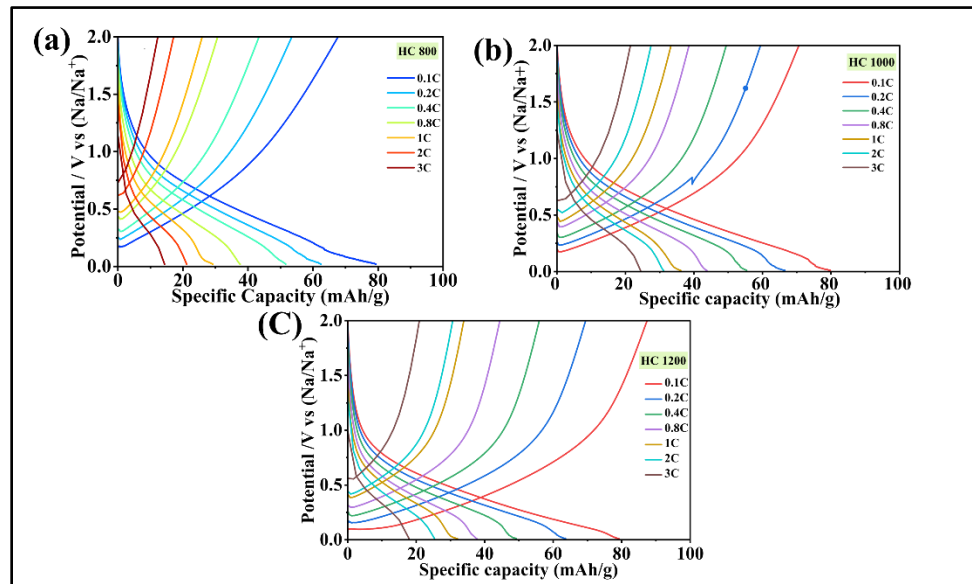


Fig. 4.10 GCD profile of (a) HC 800, (b) HC 1000, (c) HC 1000 at different C-rate.

The discharge/charge characteristics of the HC samples were further analysed at various temperatures, as shown in **Fig. 4.10**, to understand the sodium storage mechanism. As the carbonisation temperature increases, the specific discharge capacity follows a non-monotonic trend; it increases from HC 800 to reach its maximum in HC 1000 (~105 mAh/g), before significantly declining in HC 1200 (~80-90 mAh/g). This peak performance at 1000 °C is attributed to the optimised d-spacing and pore structure that facilitates maximum Na-ion intercalation. The voltage profiles for all samples exhibit two distinct storage regions. The sloping region (from 2.0 V to ~0.1 V) is associated with the adsorption of Na-ions onto surface functional groups and defects. Crucially, the plateau region, which is observed near the 0.1 V potential window, represents the intercalation of Na-ions into the graphitic nanodomains. In HC 1000, the plateau region is more prominent and flatter compared to HC 800, indicating a more ordered yet sufficiently expanded interlayer structure. However, in HC 1200, both the sloping and plateau capacities decrease due to the 'pore closure' effect and structural densification, which restricts ion accessibility. The high reversibility of the plateau region near 0.1 V in HC 1000 confirms it as the most suitable anode architecture for stable and high-capacity Sodium-ion batteries.

Table 4.2: Summary of experimental parameters and results obtained for the prepared HC.

C-rate	HC 800		HC 1000		HC 1200	
	Charging	Discharging	Charging	Discharging	Charging	Discharging
0.1C	72.46	79.35	73.63	79.83	73.54	74.3
0.2C	57.09	62.49	61.85	66.57	59.56	59.29
0.4C	46.35	51.6	51.52	55.39	45.89	46.83
0.8C	33	37.64	40.33	43.78	34.69	35.48
1C	28.06	29.18	35.11	36.16	31.19	31.94
2C	18.79	21.15	29.05	31.11	23.12	22.83

3C	13.73	14.36	22.87	24.4	17.29	16.94
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4.3.9. Rate capability

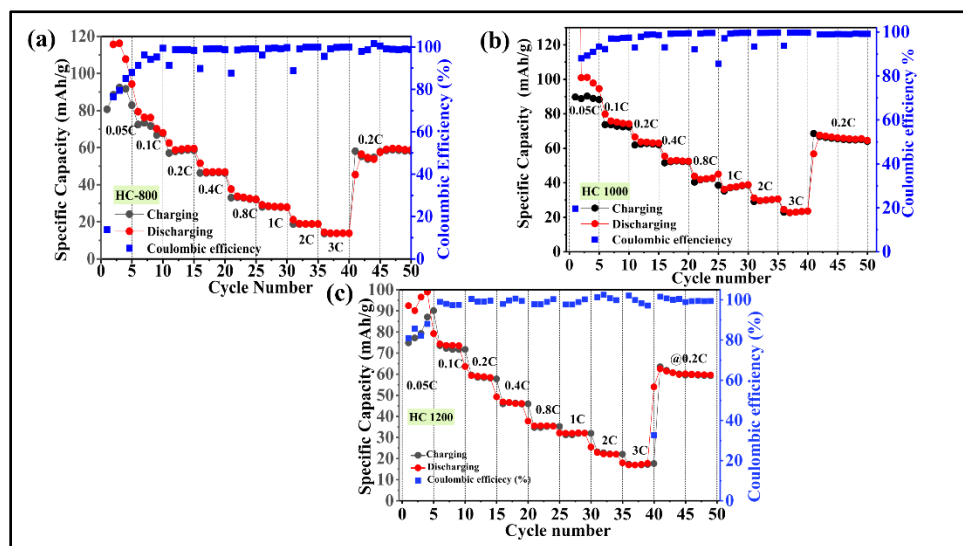


Fig. 4.11 Rate capability performance of HC electrodes (a) HC 800, (b) 1000, (c) 1200 at varying C-rates, showing capacity retention and coulombic efficiency behaviour.

Table 4.3: Electrochemical performance parameters of the prepared HC samples.

Sample	Rate capability (mAh/g)	Retention (%)
HC 800	62.49 at 0.2C	94
HC 1000	66.57 at 0.2C	96
HC 1200	59.29 at 0.2C	95

The rate performance and electrochemical stability of the HC samples were further evaluated at various current densities ranging from 0.05 C to 3 C, followed by a return to 0.2 C to assess capacity recovery

Fig.4.11 (a-c) All samples demonstrate a typical decline in specific capacity as the C-rate increases, due to the diffusion limitations of Sodium ions at high current densities. Notably, HC 1000 exhibits the most robust rate capability, delivering significantly higher capacities at each C-rate compared to HC 800 and HC 1200.

Upon returning the current density to 0.2 C (after the 3 C high-rate stress), the HC 1000 sample achieved a recovered specific capacity of 66.57 mAh/g, which corresponds to a superior capacity retention of 96%. In comparison, HC 800 and HC 1200 showed lower recovered capacities of 62.49 mAh/g and 59.29 mAh/g, with retentions of 94% and 95%, respectively. The exceptional retention and higher capacity in HC 1000 are attributed to its optimized interlayer architecture and balanced porosity, which facilitate rapid ion transport while maintaining structural integrity. Furthermore, the (CE) of HC 1000 quickly stabilizes near 100% across all C-rates, underscoring its excellent electrochemical reversibility for fast-charging applications in Sodium-ion batteries.

4.3.10. Cyclic stability

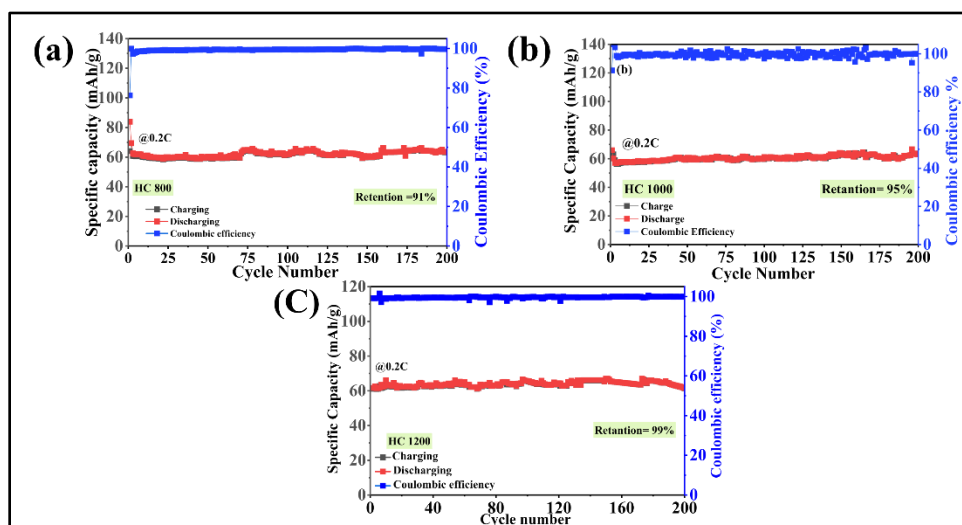


Fig. 4.12 Cyclic stability of (a)HC 800, (b) HC 1000, (c) HC 1200 at 0.2 C after 200 cycles at various temperatures.

Table 4.4: Initial capacity, 200-cycle capacity, and retention (%) of HC samples at different carbonization temperatures.

Sample	Initial capacity	Capacity after 200 cycles	Retention (%)
HC 800	69.45	63.56	91
HC 1000	65.98	63.05	95
HC 1200	61.64	61.58	99

The structural durability and cycling stability of the biomass-derived HC anodes were rigorously tested over 200 cycles at a current density of 0.2 C (**Fig.32**). The quantitative analysis, as summarized in the table, reveals that the carbonization temperature plays a decisive role in capacity retention. For the HC 800 sample, the capacity decreased from an initial value of 69.45 mAh/g to 63.56 mAh/g, resulting in a retention of 91%. The HC 1000 sample exhibited improved performance, maintaining 63.05 mAh/g from an initial 65.98 mAh/g, achieving a higher retention of 95%.

Remarkably, the HC 1200 sample demonstrated exceptional structural resilience; despite having a lower initial capacity of 61.64 mAh/g, it maintained a nearly identical final capacity of 61.58 mAh/g, yielding an extraordinary retention of 99%. This trend indicates that higher carbonization temperatures lead to a more robust and rigid carbon framework, which can effectively withstand the mechanical strain of repeated Sodium-ion insertion/extraction. Furthermore, all samples reached a (CE) near 100% within the first few cycles, signifying the formation of a stable (SEI) and minimal electrolyte decomposition. Consequently, while

HC 1000 provides a better balance of capacity and stability, HC 1200 stands out as the most structurally stable candidate for long-life Sodium-ion storage applications.

Chapter 5

Conclusion and Future Scope

The comprehensive research detailed in this thesis successfully demonstrates the viability of utilizing sustainable, biomass-derived sawdust as a precursor for synthesizing high-performance HC anode material for SIBs. Driven by the urgent need for cost-effective and abundant alternatives to conventional lithium-ion technologies, this work systematically evaluated the impact of varying carbonization temperatures 800°C, 1000°C, 1200°C. on the structural, morphological and electrochemical properties of the synthesized material. Physiochemical characterizations, including Raman spectroscopy and BET analysis, confirmed that the temperature of HC 1000°C generated an optimal non-graphitizable carbon framework. Specifically, HC 1000 exhibited the highest concentration of structural defects and active edges (indicated by an I_D/I_G ratio of 1.5). alongside a well-balanced mesoporous architecture that maximizes the active sites for sodium-ion adsorption. Electrochemical testing in half-cell configurations conclusively validated HC 1000 as the most superior anode material, delivering a peak specific discharge capacity of 105 mAh/g. Furthermore, HC 1000 demonstrated a remarkable rate capability. After enduring high-rate stress up to 3C, it successfully recovered a specific capacity of 66.57 mAh/g when returned to 0.2C, equating to an outstanding capacity retention 96%. Long-term cycling evaluations over 200 cycles at a current density of 0.2C further highlighted the structural integrity of the synthesized materials. While HC 1200 exhibited a capacity retention of 99% due to its highly rigid thermal framework, HC 1000 offered the most optimal balance of capacity and stability, maintaining a robust 63.05 mAh/g (from an initial 65.98 mAh/g) with a 95% retention rate. Additionally, all materials rapidly achieved a Coulombic efficiency approaching 100% within the initial cycles, signifying the formation of highly stable SIE layer. Ultimately, this

study empirically proves that HC 1000 as a highly scalable, stable and cost-effective anode solution for the next generation of large-scale energy storage systems.

Future scope

There is a lot of future scope to work on biomass-derived HC anode material for sodium ion battery.

- Transition from half-cell evaluations to full-cell fabrication by pairing the optimized HC-1000 anode with high-performance cathodes.
- Explore chemical activation of the raw sawdust prior to carbonization to optimize the pore size distribution for enhanced sodium-ion adsorption.
- Utilize real-time, in-situ characterization techniques, e.g., in-situ XRD, Raman, to deeply analyze structural dynamics during active charge-discharge cycles.

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