Black Phosphorus Quantum Dots as Electrolyte Additives for Secondary Batteries

A thesis
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fulfillment of the requirements for the BS-MS Dual Degree Program
By

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Certificate

This is to certify that this dissertation entitled **Black phosphorus quantum Dots as electrolyte additives for secondary batteries** towards the partial fulfillment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research, Pune represents study/work carried out by **Krushna Dilip Shewale** at Indian Institute of Science Education and Research under the supervision of **Prof. Satishchandra B Ogale**, Professor, Department of physics, during the academic year 2024-25.

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Dr. Aparna Deshpande

Thesis Expert

This thesis is dedicated to

my family, my beloved Sneha, Shubham and Chetan.

Declaration

I hereby declare that the matter embodied in the report entitled "**Black phosphorus quantum Dots as electrolyte additives for secondary batteries**" are the results of the work carried out by me at the Department of physics, Indian Institute of Science Education & Research (IISER) Pune, under the supervision of **Prof. Satishchandra B Ogale,** and the same has not been submitted elsewhere for any other degree. Wherever others contribute, every effort is made to indicate this clearly, with due reference to the literature and acknowledgement of collaborative research and discussions.

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Acknowledgement

I express my heartfelt gratitude to God Almighty for His blessings, which have enabled me to successfully complete my thesis, ″Black Phosphorus Quantum Dots as Electrolyte Additives for Secondary Batteries,″ in fulfillment of the requirements for the BSMS dual degree at IISER Pune.

First and foremost, I extend my sincere appreciation to my supervisor, Prof. Satishchandra Ogale, for granting me the opportunity to undertake this research and for his invaluable guidance, support, and patience throughout this journey. I am sincerely grateful of Dr. Aparna Deshpande for her kind guidance as my thesis expert. I am also deeply grateful to my fellow lab mates for providing a lively and collaborative work environment. A special mention goes to my mentor Dr. Swati Chaudhari for her immense help and guidance in completing this project. She supported me a lot for the thesis completion.

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Shewale Krushna Dilip

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Abbreviation

1. BP -Black Phosphorous
2. HC- Hard carbon
3. CC- Conducting carbon
4. BPQDs - Black phosphorous quantum dots
5. HC@BPQDs - Hard carbon + BPQDs
6. TEM - Transmission electron microscopy
7. HRTEM - High resolution transmission electron microscopy
8. SEM - Scanning electron microscopy
9. FESEM - Field emission scanning electron microscopy
10. XRD - X ray diffraction
11. EDS - Energy Dispersive spectroscopy
12. PVDF – Polyvinylidene Fluoride
13. NMP – N-Methyl-2-Pyrrolidone
14. CMC – Carboxymethyl Cellulose
15. SBR – Styrene-Butadiene Rubber
16. LFP – Lithium Iron Phosphate
17. SEI – Solid Electrolyte Interphase
18. EC – Ethylene Carbonate
19. DMC - Dimethyl Carbonate

Abstract

The improvement of the electrochemical performance of a rechargeable battery can be achieve by the most common and efficient technique which is adding a functional additive to the battery electrolyte, which are mostly small organic molecules, although some work has used Quantum Dots as well. In this work, black phosphorous quantum dots (BPQDs) are used as an additive to enhance the battery performance having hard carbon as an anode material. Black phosphorus is a two-dimensional layered material with unique electronic and optoelectronic properties that make it an excellent candidate to explore in energy storage applications.

The liquid-phase exfoliation method is used to obtain BPQDs using N-Methyl-2-Pyrrolidone (NMP) as a solvent. These BPQDs were incorporated in the hard carbon electrode my infiltration method. Half-cell were made to study the properties of BPQDs as an electrolyte additive. C- rate capabilities and cycling study were done along with some characterization techniques.

The addition BPQDs is shown to increase the specific capacity (4%) at 200 mA/g; the increment is seen to be significantly higher (18%) at higher C rate that is at 500 mA/g. The BPQDs appear to be good electrolyte additive and shows some remarkable properties such as facilitate the Na surface diffusion, stress management by stabilizing the SEI, enhance the Na wetting and the specific discharged capacity of Na ion battery.

Chapter 1

Introduction:

The growing energy demand, coupled with the depletion of natural resources, has raised significant global concerns regarding climate change, high increase in carbon footprint, increase in pollution and fossil fuel dependency. Due to these concern the need for renewable energy sources to meet the ever-increasing energy market demands get drastically intense. In this regard, research efforts are focused on developing cost-effective battery technologies with high energy storage capabilities to support large-scale applications.

1.1 Historical background of secondary battery

Lithium-ion battery (LIB) development began in the 1970s with Stanley Whittingham, who created the first rechargeable lithium battery, but safety issues hindered commercialization. In the 1980-decade J. B. Goodenough introduced $LiCoO_2$ as a cathode, and Akira Yoshino changed the lithium metal with graphite as the anode, making LIBs safer and practical. Sony commercialized the first rechargeable LIB in 1991, revolutionizing portable electronics. The 2000s saw advancements in cathode materials and mass adoption in EVs, led by Tesla (2008). In 2019, Whittingham, Goodenough, and Yoshino won the Nobel Prize for their contributions.

1.2 Components of secondary metal ion battery

1.2.1 Cathode

The cathode is the positive electrode of the secondary metal ion battery. Let's assume the case of Li ion battery, Li ion while discharging moves from the anode to cathode through the electrolyte, but the Li is the unstable its elemental form hence we need oxides to make the stable and homogeneous transportation of Li ion toward the cathode. The majorly used cathode materials for Li ion battery are lithium iron phosphate (LiFePO4 or LFP), lithium nickel manganese cobalt oxide (LiNiMnCoO2 or NMC), lithium cobalt oxide (LiCoO2), lithium manganese oxide (LiMn2O4). In case of Na ion battery its mainly odium-vanadium-phosphate-fluoride($Na_3V_2(PO_4)_2F_3$), Prussian blue ($Na_2Mn[Fe(CN)_6]$).

Battery capacity is predominantly depending on the cathode materials. Higher the number of Li ion inventory that can be transported from cathode to anode higher will be capacity of the battery. The gravimetric capacity, volumetric capacity, power density and energy density these all factors are depend on the cathode material. How easily and efficiently cathode donate Li ion determines the battery performance. Additionally, the 50-55% cost of the battery is depending on the cathode material. It's very important to make the cathode material cheaper and scalable to make the battery affordable and user friendly.

1.2.2 Anode

The negative electrode of the battery anode, it is again very important component of the battery after cathode. As we seen in case of cathode to donate Li or Na ion the main task of anode material is to provide space for those ions which came from the cathode. There are three predominant electrochemical storage mechanisms for anode materials: intercalation/deintercalation, conversion, and alloying. The choice of storage mechanism significantly influences the battery's overall capacity and energy density, ultimately affecting its runtime and longevity. An ideal anode material must exhibit excellent cycling stability to ensure long-term performance, especially at high current rates, while also meeting critical criteria such as safety, compatibility, and environmental sustainability. The best candidate for the anode in case of LIB is itself the Li metal anode as the theoretical specific capacity of lithium metal (Li) is 3,860 mAh/g, meaning it has the potential to store a very high amount of electrical charge per gram of material [1]. In reality it can't be used because of the dendrites formation happen by the lithium and that can ultimately tear the separator to make internal contact to cathode and eventually leads to short circuit. Also the Li is very moisture sensitive, which makes metallic Lithium very dangerous for battery application.

This problem is solved by the Graphite in the case of LIB. Graphite is highly planar in structure and possess symmetric inter-layer spacing which make it best anode material. The inter layer Spacing of graphite is 3.35 Å and the ionic radius of Li ion is 0.76 Å, hence lithium can easily intercalate inside the planes of graphite. Additionally, the Gravimetric capacity of graphite is 372 mAh/g and possess very high specific discharged capacity. These qualities make the graphite very good anode material for LIB. Carbon batteries (NIBs), graphite exhibits limited capacity due to its small inter-layer spacing (3.35 Å) and the larger ionic radius of sodium (1.02 Å) compared to lithium, making Na-graphite phase formation thermodynamically unstable and requiring high activation energy furthermore. The Na$^+$ diffusion through graphite requires overcoming a high energy barrier due to its size and weaker binding interactions, resulting in slow kinetics compare to Li ion (fig1). Therefore, we need to alter the traditional graphite by other anode material for the Sodium ion battery. Here comes the hard carbon, which solves this problem. Hard carbon possesses highly disorder noncrystalline layers of carbon stacked in a random fashion. In addition to this it has some graphitic micro crystalline structure. These all structural qualities of hard carbon helpful for Na ion storage. Storage mechanisms can be done by adsorption, intercalation and pore filling. The theoretical capacity of hard carbon hence depends on the degree of defects and it typically in the range if 300 t0 400 mAh/g.

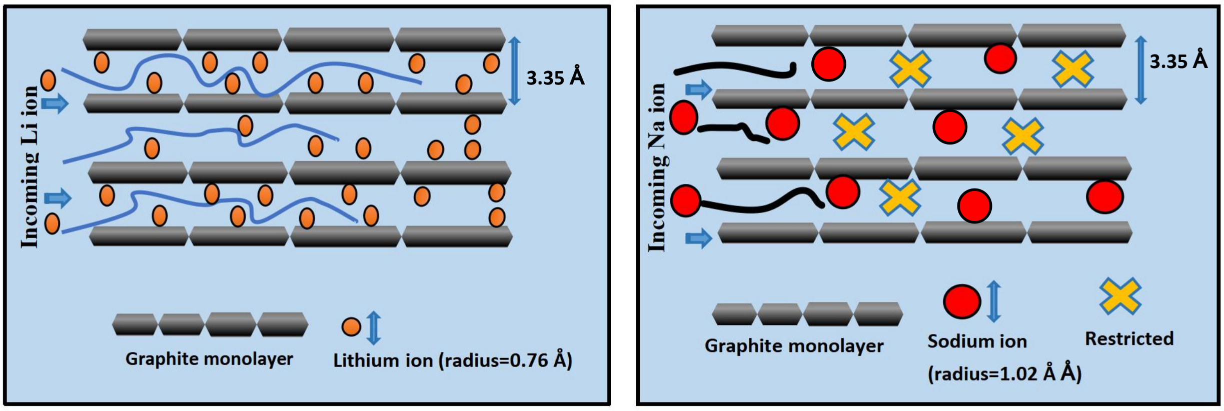

Figure 1.1 Intercalation mechanism of Li ion and Na ion in the graphite planes.

1.2.3 Electrolyte

Electrolyte is composed of solvent and the salt of corresponding metal ion. Electrolyte provides the medium for the metal ion to move through it. Electrolyte should have wide temperature range, high ionic conductivity, good chemical compatibility and wide electrochemical range for efficient working of metal ion battery. In the case of LIB liquid electrolyte is used, electrolyte used in LIB is mainly Lithium hexaflurophoshate (LiPF6) in ethylene carbonate and dimethyl carbonate solvent combination (1M LiPF6 in EC: DMC as 1:1 ratio by volume). In case of sodium ion battery sodium hexafluorophosphate salt is dissolve in diethylene glycol and dimethyl ether combined called as Diglyme (1M NaPF6 in DME: DEG). Electrolyte plays crucial role in the performance of battery. The electrolyte plays a crucial role in determining battery performance, affecting energy density, power output, cycle life, and safety. In solid-state batteries (SSBs), the liquid electrolyte is replaced with a solid electrolyte.

1.2.4 Binder

Mechanical integrity of the electrode during cycling is maintain by the binder. Binder help the active material, conducting carbon and other component to stick to the current collector efficiently. Binder can provide adhesion to active material by wander-wall forces and hydrogen bonding. Volume expansion, contraction/expansion of electrode during continuous charging/discharging causes mechanical stress on the cell that is regulated by the binder. Very low quantity of binder is used in the slurry making that is around 5% to 10% by weight with respect to active material and conducting carbon. In most of cases the binder used is polymer type due to its special properties. The convectional binder used in the LIB and SIB is Polyvinylidene Fluoride (PVDF) and the solvent used for dissolution of PVDF is N-Methyl-2-pyrrolidone (NMP). The main problem with NMP solvent is, flammability and that catches fire; additionally, PVDF can’t be used for aqueous battery due to dissolution issue. Another class of binder is Carboxymethyl Cellulose (CMC) & Styrene-Butadiene Rubber (SBR) which is used for aqueous batteries.

1.2.5 Separator

The name itself suggest it’s working principle. Separator keep anode and cathode separated to prevent short circuit. There are some important properties of separator which includes high ionic conductivity, high ionic mobility, low electronic conductivity, wide temperature and voltage range, semipermeable (allow only ions to pass) and highly porous for ionic movement through it. Conventionally used separator are majorly polymers which includes synthetic resins like polyethylene and polypropylene. Separator confirms the safety of secondary ion battery

1.2.6 Additive

Additives are the small organic molecules which we add to the electrolyte to improve the cell performance, modify the solid electrolyte interface (SEI) layer, minimize the side reaction and improve the thermal stability of electrolyte. The standard range of concentration of additives used in the electrolyte is typically 0.5-5 wt.%. Additives prevent the electrolyte degradation and eventually keeps the Li ion inventory being loss. This may lead to the increase in the capacity and energy density of the secondary battery.

1.3 Working principle of secondary battery

Let's assume a Lithium ion battery for reference, as we know secondary battery operates on the reversible movement of Li ion during multiple cycles of charging and discharging. While charging, we applied the external voltage to the battery (positive terminal to cathode and negative terminal to anode) and electrons flow from cathode to anode. That force the Li ion at cathode to migrate towards the anode which is at negative potential [fig 1.2]. Multiple reactions happened at cathode and anode during charging.

Reaction at cathode electrode

$$\mathbf{LiCoO_2 \rightarrow Li_{(1-y)}CoO_2 + yLi^+ + ye^-} \text{ -------------------(1)}$$

Reaction at the Anode

$$\mathbf{yLi^+ + ye^- + C_6 \longrightarrow Li_yC_6} \text{ --------------------------------(2)}$$

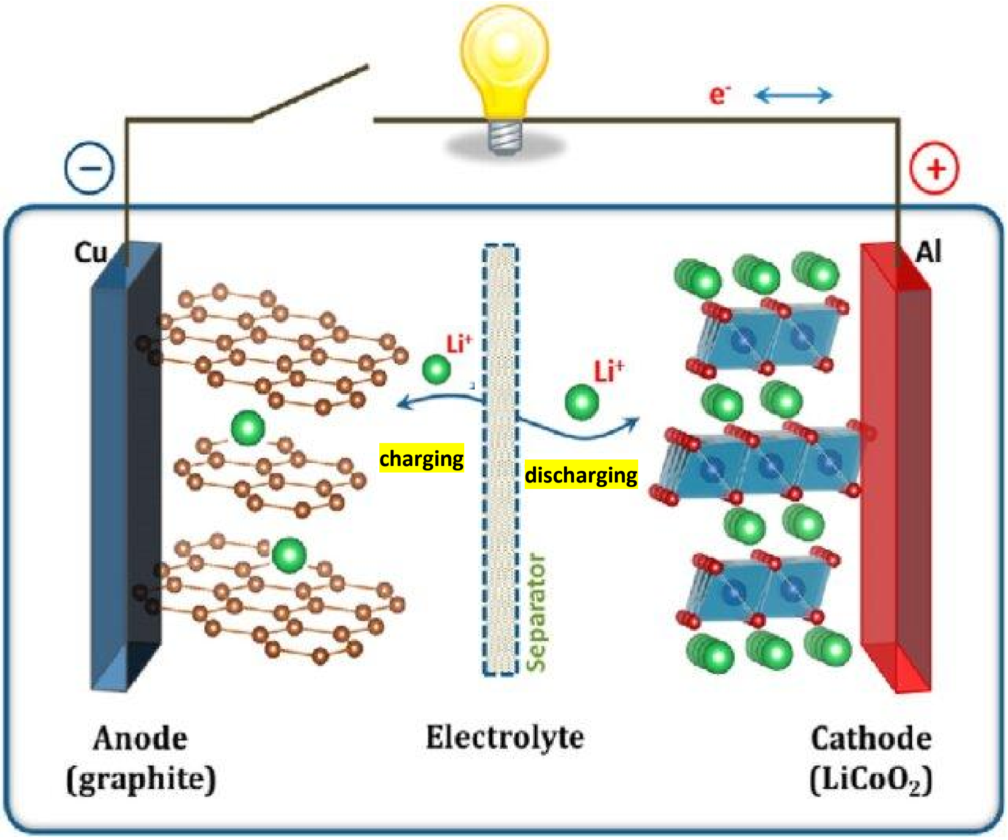

Figure 1.2 Movement of Li ion while charging and discharging

At anode when Li ion comes it is surrounded by the 6 carbon atoms and intercalation takes place. While discharging when we apply load to the battery the LiC6 at the anode again leaves the Li ion in the electrolyte to give one electron to the external circuit to get electricity. In this way trillions of electrons flows from the cathode to anode while discharging via external circuit and Li ions through the electrolyte of battery. Separator only allow the Li ions to pass through it by blocking the electron flow. Reactions happen at respective electrode during discharging is given below

Reaction at the Anode: $Li_xC_6 \longrightarrow xLi^+ + xe^- + C_6$ --------------------(3)

Reaction at cathode: $Li_{1-x}CoO_2 + xLi^+ + xe^- \longrightarrow LiCoO_2$ --------------------(4)

From Equation 1 to 4 we can see the Li ion reversible movement between two electrodes during charging and discharging cycle.

At the 1st few cycle, there is formation of passive layer on the anode surface called Solid electrolyte interphase (SEI), which is mainly form by the decomposition of electrolyte and side reaction of electrolyte with the Li ion. SEI formation may cause Li inventory lose but due to SEI layer anode surface get passive to electrolyte which can eventually prevent the further decomposition of electrolyte. Hence there is a need to optimize the SEI layer thickness for better battery performance and longer life. This can be achieving by adding some compatible additive to the electrolyte, they can me small organic molecules, nanoparticles, quantum dots, etc.

1.4 Challenges faced by rechargeable Li ion battery

The major component of lithium ion battery is itself a lithium metal. The sources of lithium are not homogeneously distributed throughout the world, it is mainly concentrated at Australia, Chile and Argentina. [5] Due to this inhomogeneous distribution, lots of factor plays essential role for Lithium ion battery such as transportation of lithium metal, geopolitical issues, international security concerns, etc. (fig 1.3). The prices of lithium metal are touching the sky due to growing demand for LIBs in Electric Vehicles (EVs) and portable devices. Addition to this, LIBs have one more serious issue of Overheating that can cause fires and explosions, especially in high-energy applications like EVs, this makes LIBs very sensitive. However, due to the increasing demand for lithium-ion batteries (LIBs) and concerns regarding lithium's cost and availability, researchers are actively investigating alternative alkali metal-ion batteries, with sodium-ion and potassium-ion batteries emerging as the most promising candidates. These elements are not only more abundant and cost-effective but also possess electrochemical properties similar to lithium, making them strong candidates for next-generation energy storage systems.

In a broad sense, battery performance is primarily influenced by the cathode, anode, and electrolyte. Various cathode materials offer excellent specific capacities, energy densities, and cycling stability. However, the anode plays a pivotal role in defining the energy storage mechanism and significantly impacts overall battery performance. There are lots of alkali metal-ion anode materials, carbon-based compounds, including soft/hard carbons (HCs) and natural/synthetic graphite (fig 1.4), are emerging as practical and cost-effective candidates due to their structural diversity, porosity, and global abundance. Instead of depending on lithium, we should focus on the sodium as a battery material and should develop new technologies for the Sodium ion batteries (SIB).

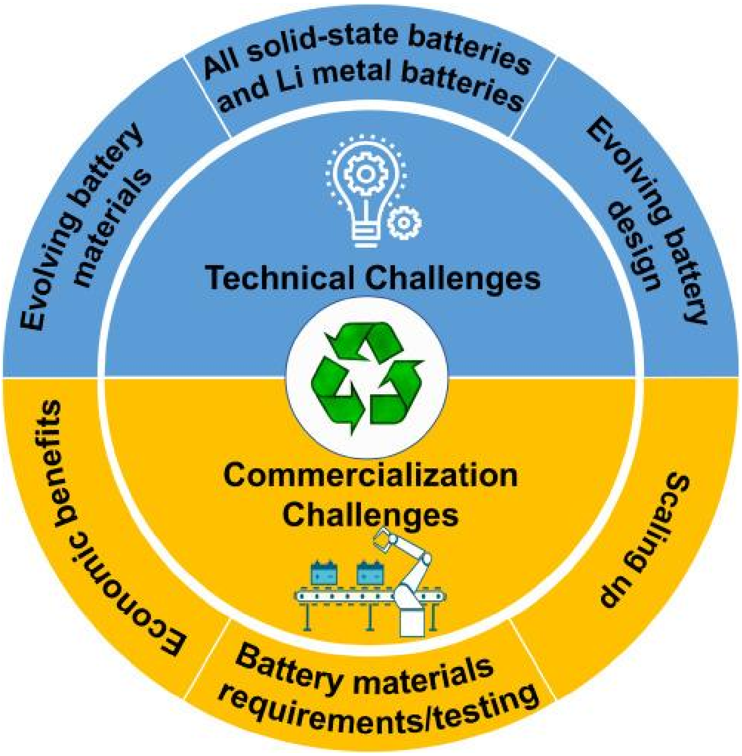

Figure 1.3 Challenges faced by the rechargeable Li ion battery

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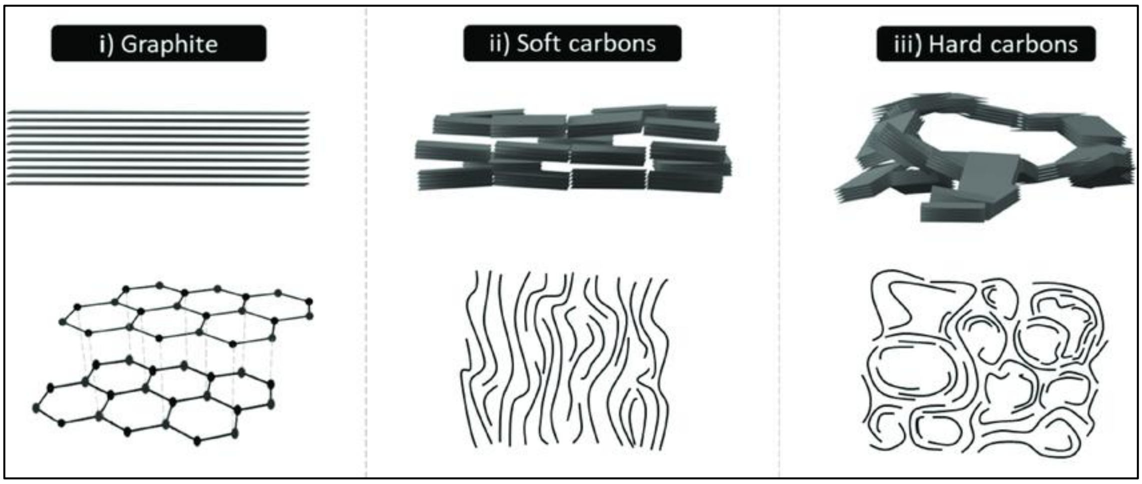


Figure 1.4 Comparison between graphite, soft carbon and hard carbon

Image ref: https://www.researchgate.net/publication/368246237

1.5 Hard carbon as an anode material

As we discussed earlier that sodium is now being used in the next generation energy storage batteries. Conventional anode for the LIB is graphite but due to some structural and intercalation behavior graphite cannot used as an anode in case of SIB. Hard carbon possess randomly oriented disorder layers of carbon atoms which forms pores in-between and some of the voids. Hard carbon has a larger spacing 3.7–4.5 Å, allowing efficient Na^+ storage. The storage mechanism of hard carbon is Pore filling and surface adsorption and very little intercalation [2] (fig4). The specific capacity of HC is around 350-400 mAh/g which is as comparable as graphite in LIB.

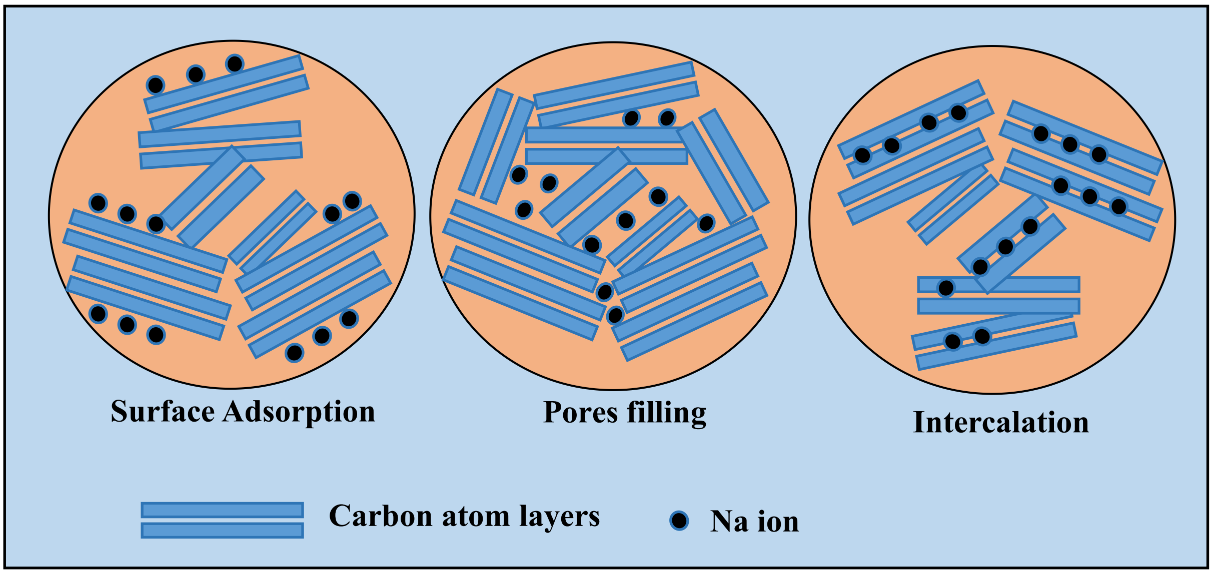


Figure 1.5 Storage mechanism of Na ion in a hard carbon

Chapter 2

Experimental techniques

2.1 Materials and chemicals

Black Phosphorous powder, Hard carbon, conducting carbon (super P), N-Methyl-2-Pyrrolidone (NMP), Polyvinylidene Fluoride (PVDF), Ethylene carbonate (EC), Dimethyl carbonate (DMC) Sodium hexafluorophosphate (NaPF6), Sodium metal, Aluminum foil, Wattman separator, Deionized water,

2.2 Methods and Technique

To perform whole experiment few techniques are used which are mention below. Experiment contains synthesis of black phosphorous quantum dots, electrode making for coin cell, coin cell fabrication, cell testing (cycling study)

2.2.1 Synthesis of Black Phosphorous Quantum dots

Black phosphorous Quantum dots are synthesis by liquid phase exfoliation technique [5]. To make quantum dots we gone through multiple steps, in which black phosphorous powder is exfoliated in a systematic manner to fine and superior quantum dots. Following techniques are used for the effective exfoliation of BPQDs.

Techniques used for BPQDs synthesis:

1. **Grinding**

10 mg of black phosphorous (BP) powder is ground in the mortar inside the glow box for 10 to 15 minutes. This is done in the inert atmosphere of Argon gas. Grinding of Bulk BP powder causes larger particles of BP turns into the smaller ones to make fine powder. That makes easier for the further exfoliation. Later, around 10 ml N-Methyl-2-Pyrrolidone (NMP) added in this fine powder and taken out from the glow box for further exfoliation.

2. **Probe sonication**

The solution of BP powder and NMP is then subjected to the exfoliation by probe sonication to further reduce down the size of bulk BP. In a probe sonication a high-frequency electrical signal is converted into mechanical vibrations. These vibrations generate ultrasonic waves (20–40 kHz) in the liquid medium that generate a high shear force that break particle into smaller size. While doing this the localized temperature becomes so high that may damage sample. To avoid this, we kept the solution inside the ice bath to regulate the temperature of solution. This Probe sonication is carried out for 6 hrs. in the described condition. Probe sonication transform the bulk powder into smaller flakes of few layer thick sheet like structure.

3. **Bath sonication**

Once the probe sonication done, the solution is subjected to the bath sonication for about 6 hrs. again for further exfoliation. Bath sonication is again done in the ice bath having DI water as a medium for efficient exfoliation. Ice bath is important to regulate the heat generated during entire process. The final result of bath sonication causes the further breakdown of Nano-sheets into smaller particle of quantum size. Probe sonication and bath sonication forms the particle which having size distribution from micro size particles to quantum sized particle.

To separate out these we need to use centrifuge technique.

4. **Centrifuge technique**

Once the exfoliation done by probe and bath sonication, the solution is subjected to the centrifuge machine for the separation of smaller particle from larger ones. Solution is filled in two centrifuge tubes in equal proportion and subjected to the 7000 rpm for 20 minutes. Heavier particle settled down at the bottom of tube and the smaller size particle remain in the remaining part of the solution which carefully removed.

The removed solution is again subjected to the centrifugation for 12000 rpm to further separate out the quantum dots from the solution. Higher rate of centrifuge causes efficient separation of BPQDs from the nanoparticle and Nano sheets of black phosphorous.

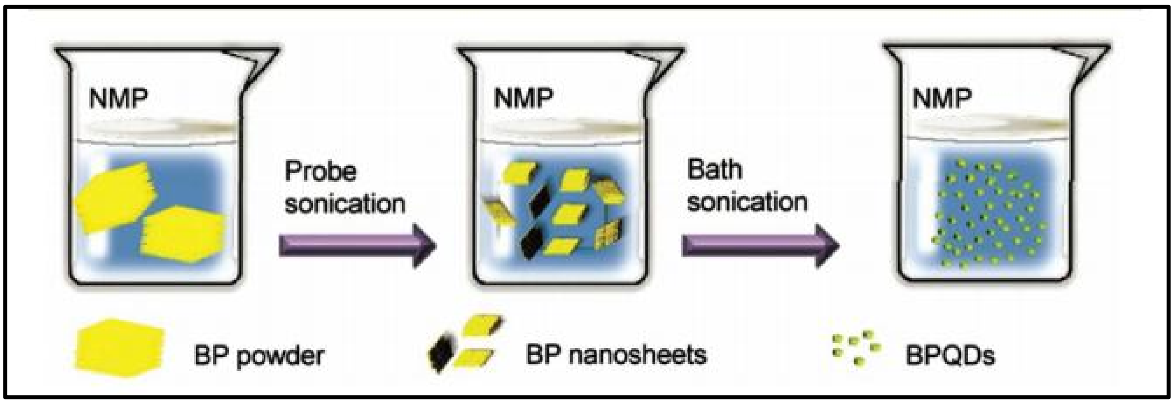


Figure 2.1 Synthesis of BP quantum dots from BP powder by liquid phase exfoliation.

Image Ref: https://www.mdpi.com/1999-4923/13/9/1344

2.3 Coin Cell fabrication

2.3.1 Electrode making

To make electrode of hard carbon, we need to go through from few steps [6], which includes slurry making, coating, drying, calendaring, electrode cutting, etc.

1. **Slurry making**

Slurry preparation is crucial for achieving a homogeneous electrode coating. The composition and mixing process determine the electrode's conductivity, adhesion, and electrochemical performance. Composition ratio of hard carbon: conducting carbon (super P): binder (PVDF) for the slurry is 8:1:1 by weight. Binder ensures the proper adhesion to the current collector. Initially PVDF is mixed with the NMP in the *Kaku Hunter* machine, simultaneously Hard carbon and Conducting carbon (CC) mix to make homogeneous mixture. Once both get mixed, the mixture of HC and CC is added to the PVDF and NMP solution to make slurry. The final slurry should be homogeneous and viscous to make uniform and superior electrode.

2. **Slurry Coating**

After slurry preparation, the slurry is deposited onto carbon coated aluminum foil, which acts as the anode current collector, to complete the procedure for coating. In lab-scale research, the doctor blade approach is usually utilized for coating, whereas in industrial settings, slot-die or spray coating techniques are employed. The necessary mass loading, typically 1-3 mg/cm2, is achieved by controlling the electrode thickness. To get rid of extra solvent before processing, the electrode is pre-dried at 80-120°C in air or vacuum after coating. To get rid of any remaining moisture and solvents, the electrode is vacuum-dried for 10–12 hours at 120–150°C once the initial drying is finished. For the reason to avoid adverse responses while the battery is running, this step is important.

3. **Calendaring and Cutting**

The dry electrode is next put through a rolling press at a regulated pressure in a process known as calendaring. This procedure improves electrical conductivity, increases electrode density, and strengthens the bond between active materials. In order to balance mechanical integrity and electrochemical performance, the compression ratio is carefully adjusted, usually lowering the electrode thickness from 50–100 µm to 30-70 µm.

Depending on the kind of cell, the electrodes are cut into the proper shapes after calendering. Circular discs (16 mm in diameter) are punched for coin cells. Before cell construction, the cut electrodes are kept in a vacuum oven at 120°C for at least 12 hours to stop moisture absorption. This is done after they have been weighed to ensure consistent mass loading.

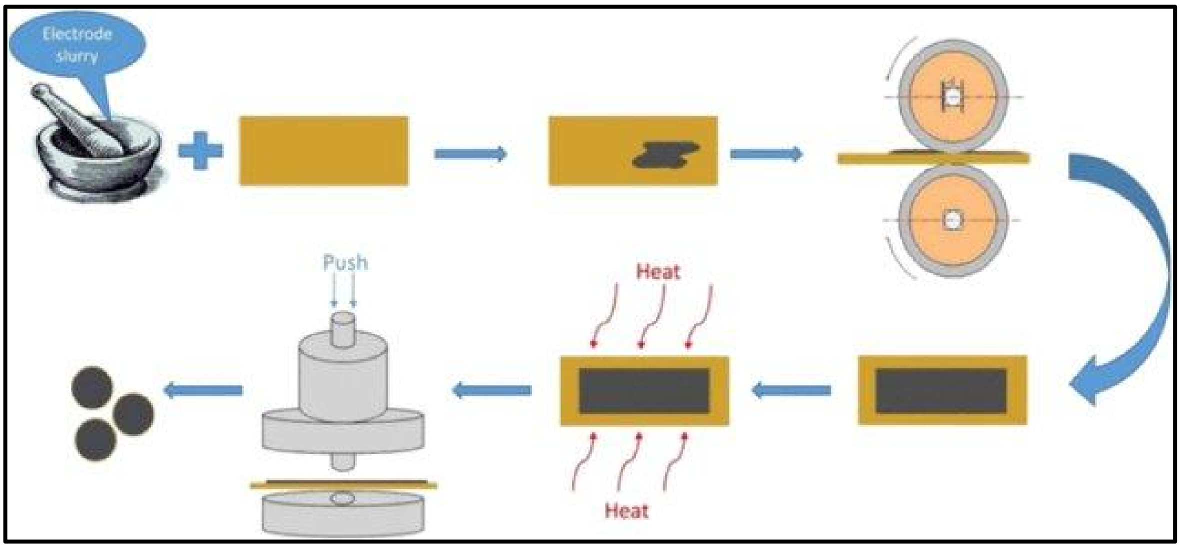


Figure 2.2 Roadmap to make electrode from active material slurry

2.3.2 Electrode Modification

Two Hard carbon electrode chosen for the coin cell fabrication having similar weight. One is modified by applying infiltration of black phosphorous quantum dots solution over it (fig 5) and one keep as it is. The BPQDs in the NMP were used for the infiltration. Around 120 µL of the solution is used for infiltration. This overall process is carried out inside the glove box in the inert atmosphere. This assembly is then kept over the heater at 80°C to remove the solvent. The whole assembly is dried over 24 hrs. to get rid of NMP solvent. We kept it at 60 degrees for 18 hrs and then increase the temperature around 80 degrees. To get systematic drying of electrode. We named the modified electrode as HC@BPQDs.

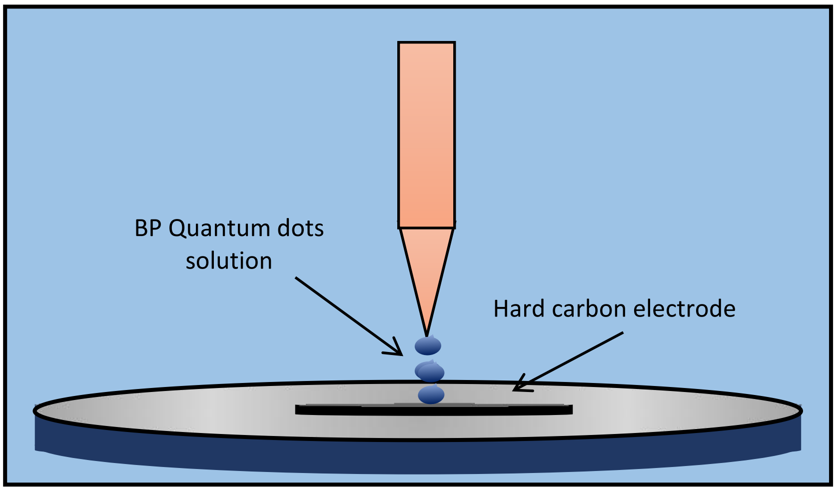


Figure 2.3 Infiltration of BPQDs solution on the hard carbon electrode

2.3.3 Preparation of Coin cell

Once the hard carbon electrode has been prepared, the next step is to assemble a **coin cell** (typically CR2032 which means 20 mm diameter and 3.2 mm thick) for electrochemical testing. Coin cell preparation involves several steps which includes electrode drying, cell assembly in a glovebox, electrolyte addition, sealing, and testing

- **Electrode Preparation**

Before cell assembly, the fabricated hard carbon electrodes must be thoroughly dried to remove any residual moisture and solvent. This step is essential because moisture can react with the electrolyte, leading to unwanted side reactions and gas evolution. The electrodes are kept in a vacuum oven at 110-150°C for at least 12 hours. After drying, they are kept in an argon-filled glovebox (O_2 & H_2O levels < 0.1 ppm) to prevent contamination.

- **Coin Cell Assembly in an Argon Glovebox**

The whole process of coin cell making is done inside the glovebox in the inert atmosphere of argon to avoid electrode contamination and oxidation. To assemble coin cell typically we need working electrode which is hard carbon having carbon coated aluminum foil, counter electrode which is sodium metal itself, Wattman separator, electrolyte which contains sodium metal ion conventionally 1M $NaPF_6$ in EC: DMC (1:1 v/v)

To make coin cell we typicality use stainless steel cases and spacer. Spacer are used to make cell compact and fix. Initially positive case kept on which one 0.5 mm spacer is placed, surface of sodium metal need to clean to get rid of oxidation and contamination on the surface. Then Na metal electrode is placed on the spacer. Ones the counter electrode fixed we assemble the Wattman separator on the sodium metal. After then we add 120 µL electrolyte uniformly over separator to make proper wetting. Now we placed our working electrode which is hard carbon over the separator. Once it has done we place one more 0.5 mm spacer and spring to keep proper compactness of cell and finally placed the negative case to close the cell. Then the cell is subjected to the high pressure to make it close and ensure that there us no any electrolyte linkage.

In this way, we made two cell one with bare hard carbon electrode and one is modified hard carbon electrode. These cell set for further electrochemical study.

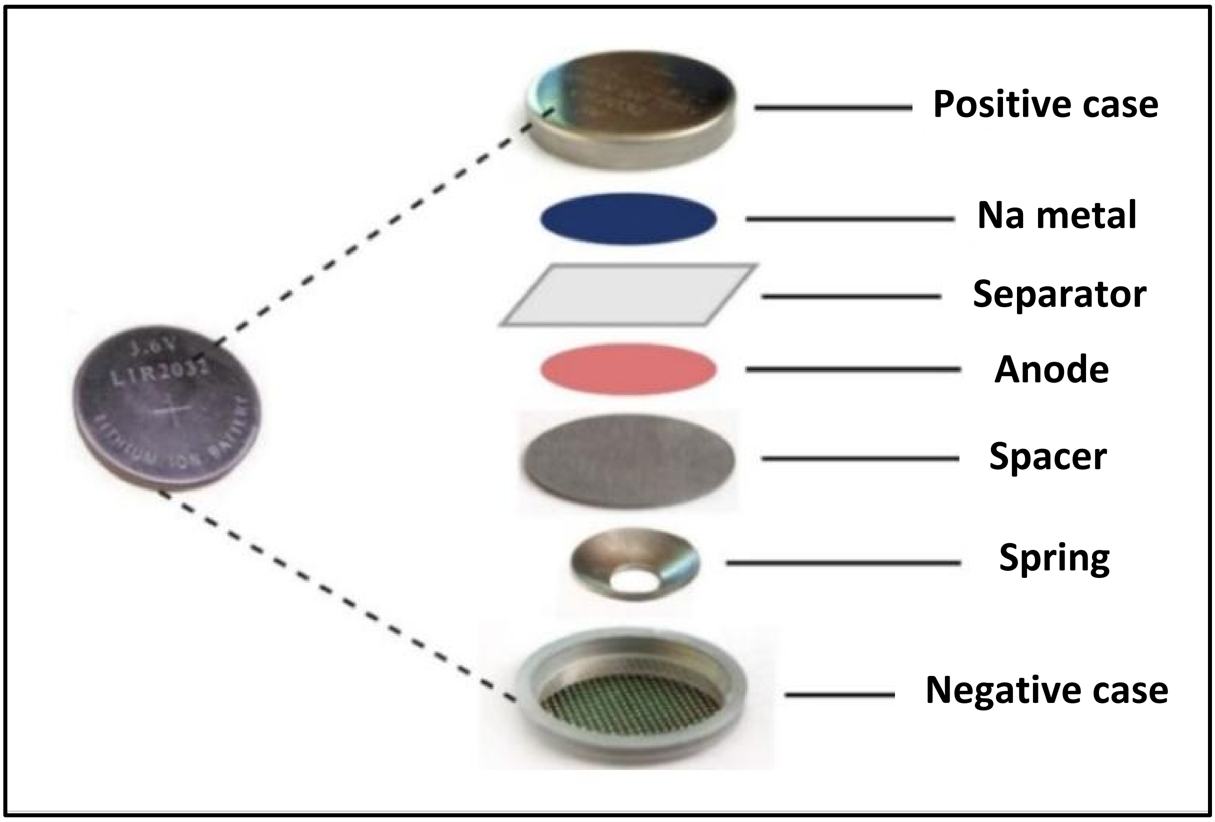


Figure 2.4 Components of 2032 Coin cell and its assembly

Image ref: https://www.researchgate.net/publication/348416345

2.4 Experimental techniques

2.4.1 Transmission electron microscopy (TEM)

Transmission Electron Microscopy (TEM) is an advanced imaging technique in which a beam of electrons passes through a sample to produce high-resolution images. While TEM operates on principles similar to those of light microscopy, it utilizes electrons instead of light. The key advantage of TEM over optical microscopy is its ability to surpass the resolution limitations imposed by the wavelength of light, as electrons have much shorter wavelengths. This allows TEM to generate highly magnified, detailed images.

In TEM, a high-energy electron beam is directed at the sample, and its interaction with the atomic structure provides valuable information about crystal structure, morphology, grain boundaries, degree of crystallization, and strain distribution. High-Resolution TEM (HRTEM) enables an even more detailed analysis, offering insights into the quality, size, shape, and density of quantum wells and quantum dots. It is particularly effective for studying nanoscale structures such as nanoparticles, nanowires, and quantum materials, revealing precise details about their lattice fringes and atomic arrangements. This technique is widely used in materials science, semiconductor research, nanotechnology, and biological imaging.

To facilitate effective electron transmission, TEM requires ultra-thin samples. Carbon-coated TEM grids are commonly used for this purpose, as they allow partial electron permeability. The electron beam, emitted from the cathode of an electron gun, is accelerated toward the anode, while a condenser aperture filters out high-angle electrons, refining the beam into a narrow, focused stream. When the beam interacts with the sample, electron transmission varies depending on the sample's thickness and electron transparency. The objective lens then focuses the transmitted electrons to generate an image, which is further magnified by the projector lens. Finally, when the image reaches a phosphor screen, visible light is emitted, allowing structural visualization. TEM and HRTEM analyses were performed using a JEM 220 FS Joel 200kV microscope.

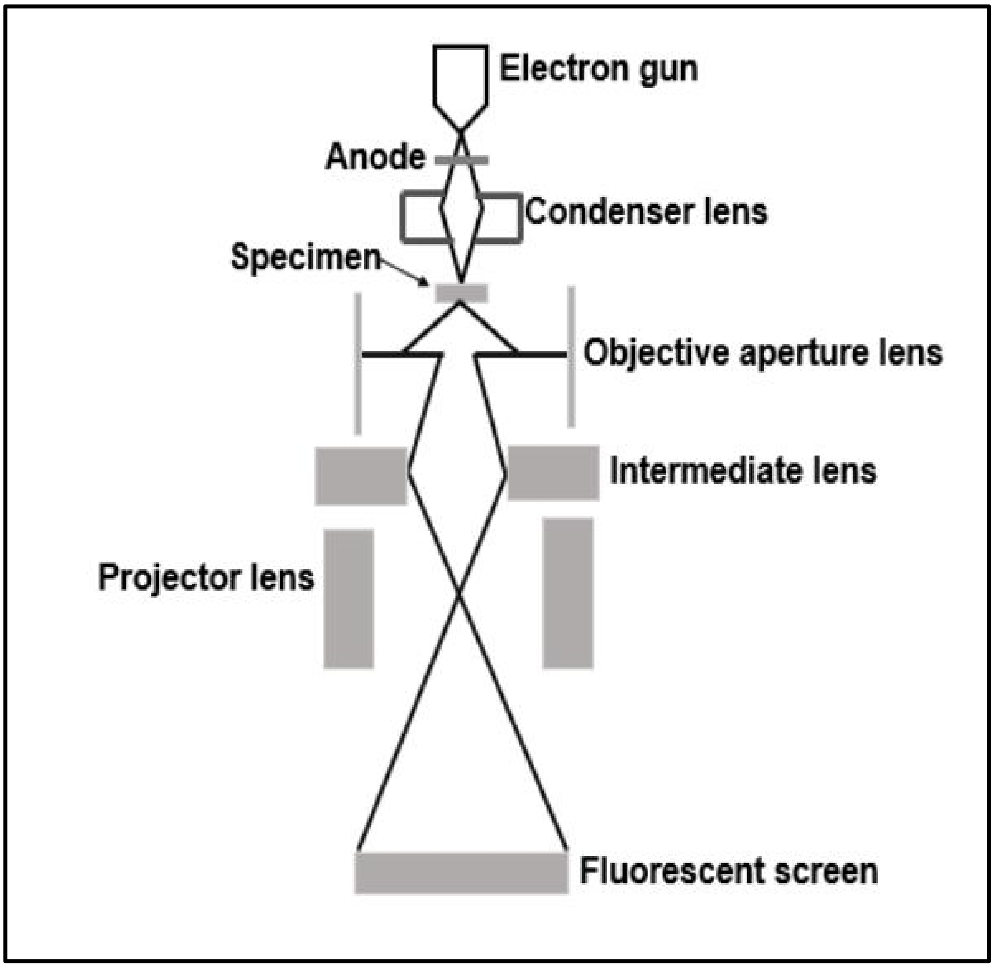


Figure 2.5 Schematic illustration of TEM

2.4.2 X-ray diffraction

1. X-ray Diffraction (XRD) and Its Working Principle

X-ray Diffraction (XRD) is a commonly used technique for the characterization, non-destructive analytical technique that helps determine the crystalline structure, phase composition, and unit cell parameters of a material. By analyzing the diffraction patterns of X-rays interacting with a sample, XRD provides crucial insights into the lattice parameters, crystal size, preferred orientation, strain, and defects within a material. This technique plays a vital role in materials science, chemistry, physics, nanotechnology, and pharmaceuticals, as it allows researchers to understand the atomic arrangement and structural integrity of different materials.

2. X-ray Properties and Their Interaction with Crystals

X-rays are high-energy electromagnetic waves with wavelengths ranging from 0.01 to 10 nm, which is comparable to the inter-planar spacing in a crystalline lattice. This similarity in scale makes X-rays highly effective for investigating the atomic structure of materials. X-ray diffraction (XRD) operates on the principle of wave-particle duality, where X-rays interact with the electron clouds of atoms, resulting in diffraction patterns that provide structural insights.

In a standard XRD setup, X-rays are produced in a cathode-ray tube by bombarding a metal target, typically copper (Cu) or molybdenum (Mo), with high-energy electrons, generating characteristic X-ray radiation. To ensure precise analysis, these X-rays are filtered to produce a monochromatic beam of a single wavelength. A collimator is then used to focus and direct the X-ray beam onto the sample.

Diffraction Process and Bragg's Law

When the monochromatic X-ray beam interacts with the sample, the incident X-rays scatter in various directions based on the electron density distribution within the crystal lattice. Some of these scattered waves undergo constructive interference, while others cancel out due to destructive interference. Constructive interference occurs when X-rays reflected from parallel atomic planes satisfy Bragg's Law, leading to the formation of distinct diffraction patterns, which is expressed as:

$$n\lambda = 2d\sin\theta$$

Where,

- n = integer representing the diffraction order,
- λ = wavelength of the incident X-ray,
- d = spacing between atomic planes (interplanar spacing),
- θ = angle of incidence (also called the Bragg angle).

When this condition is met, the reflected waves reinforce each other, producing an intense diffraction peak. The position and intensity of these peaks help in determining the phase composition, lattice constants, and atomic arrangement of the sample.

- **Applications and Importance of XRD**

- Phase determination: Determining the different crystalline phases present in a material.
- Lattice parameter measurement: Understanding the atomic-scale spacing and structure.
- Crystallite size estimation: Evaluating the size of crystal domains within polycrystalline samples.
- Preferred orientation analysis: Detecting if crystals are aligned in a particular direction.
- Strain and defect analysis: Identifying internal stresses, dislocations, and structural defects.

Modern XRD instruments feature advanced detectors and automated data processing systems, improving both accuracy and efficiency. Various techniques, including powder XRD, single-crystal XRD, grazing incidence XRD, and in-situ XRD, enable researchers to analyze a diverse range of materials, such as metals, ceramics, polymers, semiconductors, and biological samples.

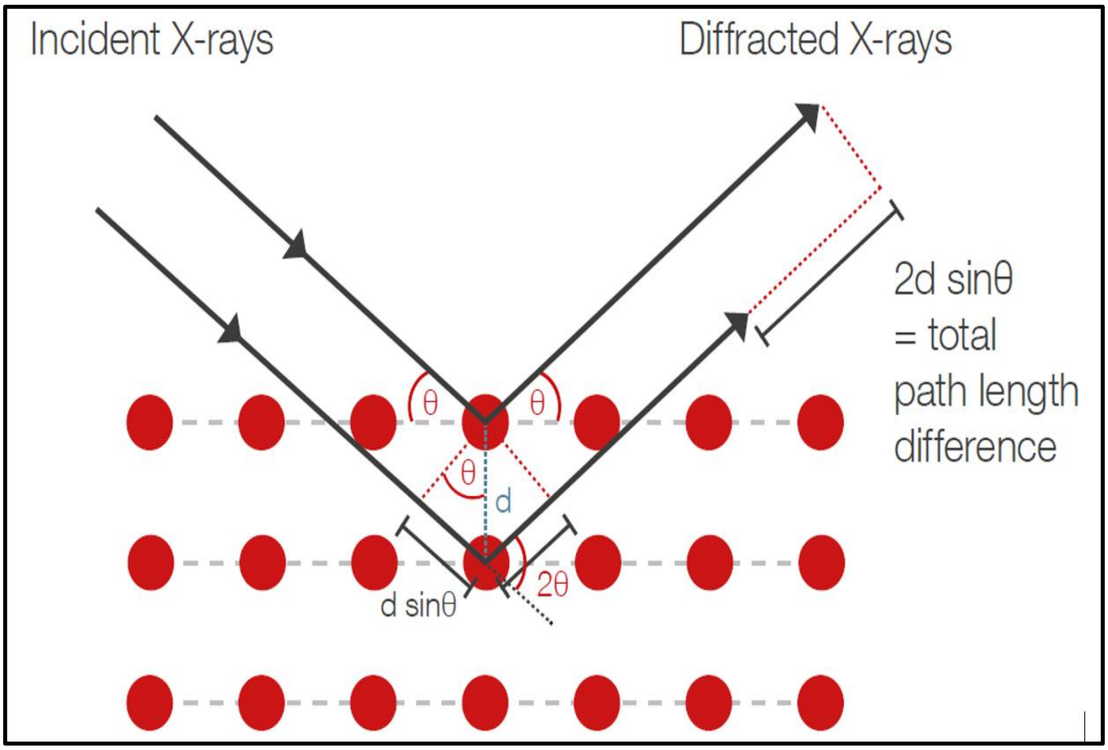


Figure 2.6 Schematic illustration of Bragg's diffraction

Image ref: https://wiki.anton-paar.com/en/x-ray-diffraction-xrd/

2.4.3 Field Emission Scanning Electron Microscopy (FESEM)

Field Emission Scanning Electron Microscopy (FESEM) is a high-resolution imaging technique used to analyze the surface morphology and topography of materials at the nanoscale. Unlike traditional optical microscopy, which uses visible light, FESEM utilizes a focused beam of high-energy electrons to produce detailed images. Compared to conventional Scanning Electron Microscopy (SEM), FESEM provides enhanced imaging precision by reducing electrostatic distortions and capturing finer surface details. This makes it a crucial tool in materials science, nanotechnology, and biological research.

1. Electron Beam Generation and Interaction with the Sample

In FESEM, electrons are emitted from a field emission cathode within an electron gun due to the application of a strong electric field, which extracts electrons from the sharp tungsten tip. These primary electrons are then accelerated under high voltage (typically 1–30 kV) and guided toward the sample using electromagnetic lenses within a vacuum column.

Upon interacting with the sample surface, the focused electron beam induces the emission of secondary and backscattered electrons, which provide critical information about the material’s surface structure, composition, and texture. The characteristics of these emitted electrons, including their number, velocity, and angular distribution, depend on the sample’s topography, conductivity, and composition.

2. Detection and Image Formation

The secondary electrons generated from the sample are collected by a detector, which converts them into an electrical signal. This signal is then amplified and processed to produce a high-resolution image. Since FESEM operates under ultra-high vacuum conditions ($\sim 10^{-7}$ Torr), electron scattering and loss are minimized, ensuring greater imaging precision.

3. Advantages of FESEM Over Conventional SEM

FESEM provides several distinct advantages over traditional SEM, making it a preferred technique for ultra-high-resolution imaging:

- Higher Resolution – The spatial resolution of FESEM is significantly better than optical and conventional electron microscopes, with a resolution limit reaching 0.017 nm. This allows for the detailed visualization of nanostructures.
- Minimal Electrostatic Distortions – Since the electron beam is generated using field emission rather than thermionic emission, image blurring due to electrostatic interactions is significantly reduced.
- Sharper and Clearer Surface Details – The use of a narrow electron beam results in crisper images, capturing fine topographical and morphological details at a nanometer scale.
- Lower Electron Beam Energy Requirement – Unlike SEM, which requires higher accelerating voltages, FESEM can operate efficiently at lower voltages (0.5–5 kV), making it suitable for imaging sensitive, non-conductive, or beam-sensitive materials.
- Enhanced Depth of Field – FESEM provides an excellent depth of field, making it highly useful for imaging irregular or rough surfaces.

4. Applications of FESEM

FESEM is an essential tool in various scientific and industrial applications, including:

- Nanotechnology – Characterization of nanomaterials, nanoparticles, and nanostructured surfaces.
- Materials Science – Investigating the microstructure, porosity, and surface properties of metals, ceramics, and polymers.
- Biological Studies – Imaging biological specimens such as cells, tissues, and biofilms without extensive sample preparation.
- Semiconductor Industry – Quality control and failure analysis of microchips, thin films, and integrated circuits.
- Forensic Science – Analyzing gunshot residue, fibers, and micro-particles in forensic investigations.

Field Emission Scanning Electron Microscopy (FESEM) has transformed high-resolution imaging by enabling precise analysis of nanoscale surface features. Utilizing a field emission electron source, it reduces distortions and offers superior spatial resolution compared to conventional SEM. FESEM is widely applied in nanotechnology, materials science, electronics, and biomedical research, making it an essential tool for examining fine structural details in modern scientific studies.

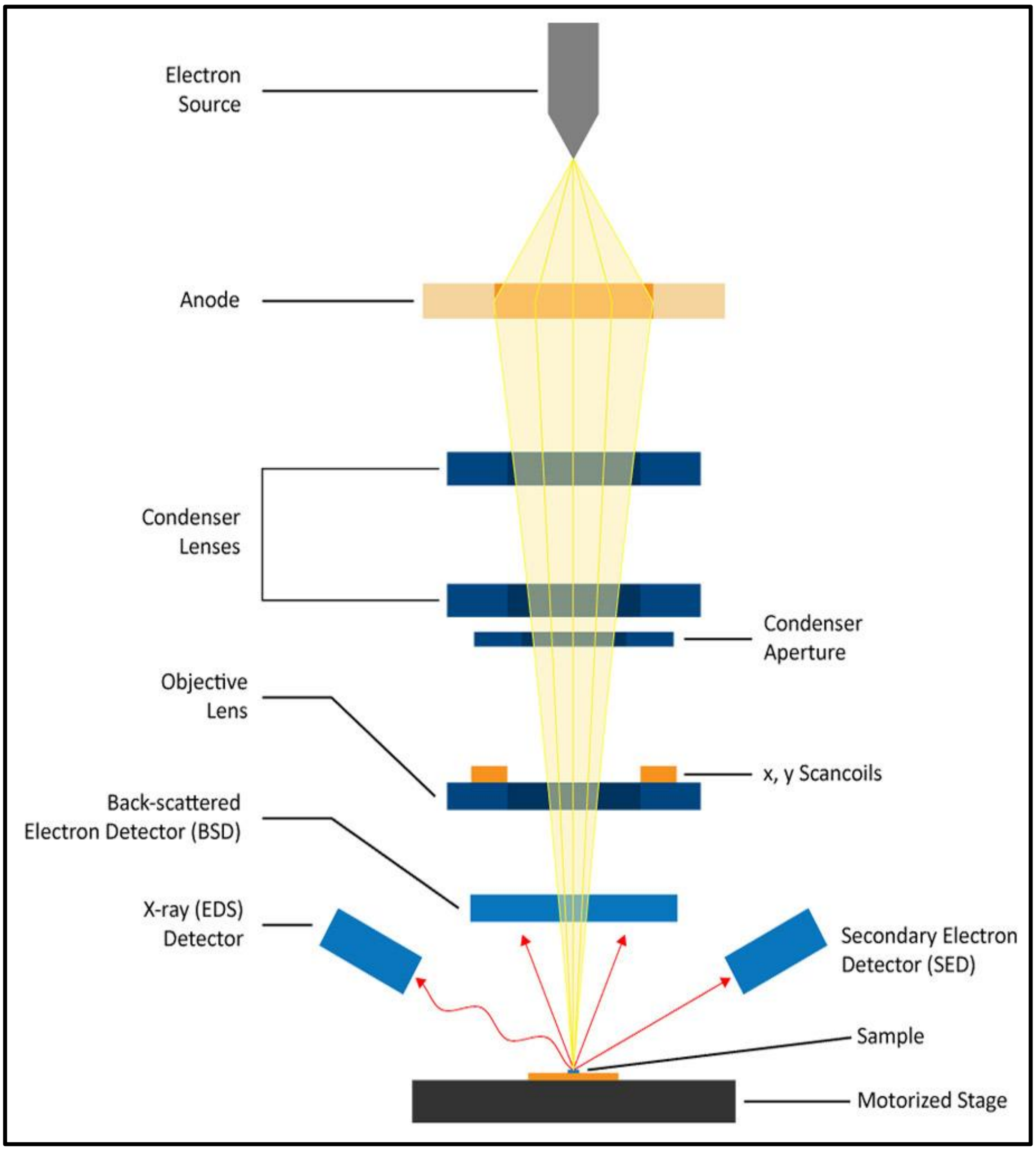


Figure 2.7 Schematic for illustration of field emission scanning electron microscopy

Image ref: https://www.nanoscience.com/techniques/scanning-electron-microscopy/

2.4.4 Energy Dispersive Spectroscopy (EDS)

Energy Dispersive Spectroscopy (EDS) is a technique used to determine the elemental composition of a material. It is often used along with Scanning Electron Microscopy (SEM) or Field Emission Scanning Electron Microscopy (FESEM) to analyze the chemical composition of a sample. It is very useful to identify the presence of different elements in the sample.

Working principle of EDS Works

- A high-energy electron beam is focused on the sample.
- This interaction causes X-rays to be emitted from the sample.
- Each element in the sample emits X-rays with unique energy levels.
- The detector in the EDS system collects these X-rays and identifies the elements present.

Analysis of EDS data gives following insights

- Which elements are present in a sample (e.g., Carbon, Oxygen, Sodium, etc.).
- Relative amounts of each element (in atomic % or weight %).
- Presence of impurities or unwanted elements.
- Distribution of elements across the sample.

Application of EDS in Hard Carbon Analysis

- Confirms that the sample is mainly carbon.
- Identifies the presence of oxygen or other elements, which may affect battery performance.
- Helps detect impurities that could influence electrical conductivity and cycling stability.

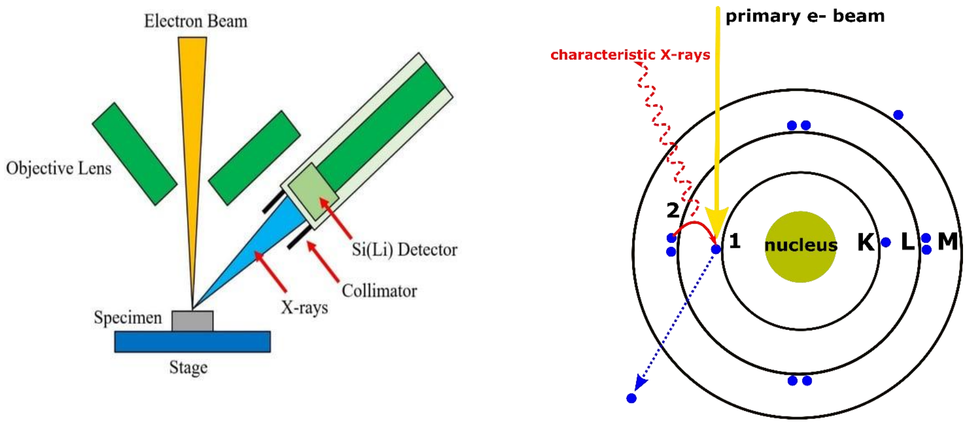


Figure 2.8 Schematic representation of EDS technique

Image ref: https://www.creative-biostructure.com/eds-analysis.htm

2.4.5 Electrochemical characterization

Charge/Discharge measurement of coin cell

Charge-discharge testing of coin cells is an essential electrochemical method for assessing battery performance. It yields critical parameters such as capacity, efficiency, cycle stability, and internal resistance, all of which play a vital role in analyzing the battery's behavior and long-term degradation.

- **Capacity**

The Capacity is the total amount of electron flow from the one electrode to other during either charging or discharging. Faraday's law gives the explanation for the theoretical capacity of battery.

Formula for the capacity of cell is as follows,

$$\boxed{\text{Theoretical capacity} = nF/3.6*Mw\ (\text{mhA/g})}$$

Where,

n = Number of charge carrier

F = Faraday constant (C/Mol)
Mw = Molecular weight of active material (g/Mol)

- **Specific capacity** is also considering as an important parameter of charge discharge testing.

It is defining from the graph of voltage vs time in which we charge and discharge the cell at constant current. Unite for the specific capacity is mAh/g.

Formula for the specific capacity is given as follows,

$$\boxed{\text{Specific capacity} = I*t/m \quad (\text{mAh/g})}$$

Where,
I = current (mA)
t = Time (hrs.)
m = mass of active material (grams)

- **Energy density**

Energy density is defining as a maximum amount of energy stored per unit weight of a battery. The formula for the energy density is as follows,

$$\boxed{\text{Energy density} = I*t * V \quad (\text{Wh/kg})}$$

Where,
I = current (mA)
t = Time (hrs)
V = Voltage (volt)

- **Power density**

Power density is the rate at which the battery can deliver the energy. This parameter actually gives idea about how fast battery can provide energy. The formula for the power density is given as follows,

$$\boxed{\text{Power density} = E/t \quad (\text{W/kg})}$$

Where,
E = Energy density Wh/Kg)
t = Time (hrs.)

- **Columbic efficiency**

Columbic efficiency represents the ratio of the total charge extracted from a battery to the total charge supplied during a full charge-discharge cycle. A value below 100% indicates irreversible capacity loss, which can arise due to multiple factors such as active material dissolution into the electrolyte, trapping of charge-carrying ions within the anode structure, or unwanted side reactions occurring during cycling. These losses contribute to the gradual degradation of battery performance over time.

- **Cycling stability**

Cycling stability is a key parameter that reflects the battery's durability over repeated charge-discharge cycles. It is typically evaluated by plotting specific capacity against the number of cycles. A gradual decline in capacity over time indicates performance degradation, which may result from electrolyte decomposition, electrode structural damage, or the dissolution of active material into the electrolyte. Long-term cycling stability is crucial for practical applications, as it determines the lifespan and reliability of the battery.

- **Rate capability**

It shows the ability of an electrode material to maintain its capacity under varying current densities. This is evaluated by conducting charge-discharge tests at different current rates (C-rates). A material with excellent rate capability will retain a high capacity even at fast charge-discharge rates, signifying efficient ion transport and minimal polarization effects. Poor rate performance, on the other hand, indicates sluggish reaction kinetics and high internal resistance, which can hurdle the battery's ability to provide power quickly. Understanding rate capability is particularly important for applications requiring fast energy delivery. such as electric vehicles and electronics devices.

2.4.6 Software used

- **Origin Software**

Origin software is exceptionally convenient for plotting graphs of data of charge and discharge cycles of cells. It helped in the plotting of cycling data, rate capabilities data and the data of individual cycles.

- **ImageJ Software**

This software is highly beneficial for computing interlayer and interatomic distances from TEM images of crystalline lattices. Additionally, it aids in enhancing image quality by minimizing background noise.

- **Battery Testing Software (BTS)**

This software mainly used for testing the cells performance in charge and discharge cycles. It provides idea of specific capacity (charge and discharge), coulombic efficiency, Energy density, power density, and various other parameter related to the battery performance.

Chapter 3

Experimental Results

3.1 TEM

3.1.1 TEM images for Hard Carbon

TEM images of Hard carbon given in the figure 3.1. The distorted structure of hard carbon can be seen in the image. Carbon planes are randomly oriented unlike of graphite planar structure. The inter-planar spacing (d-spacing) of hard carbon is around 0.26 nm to 0.27 nm

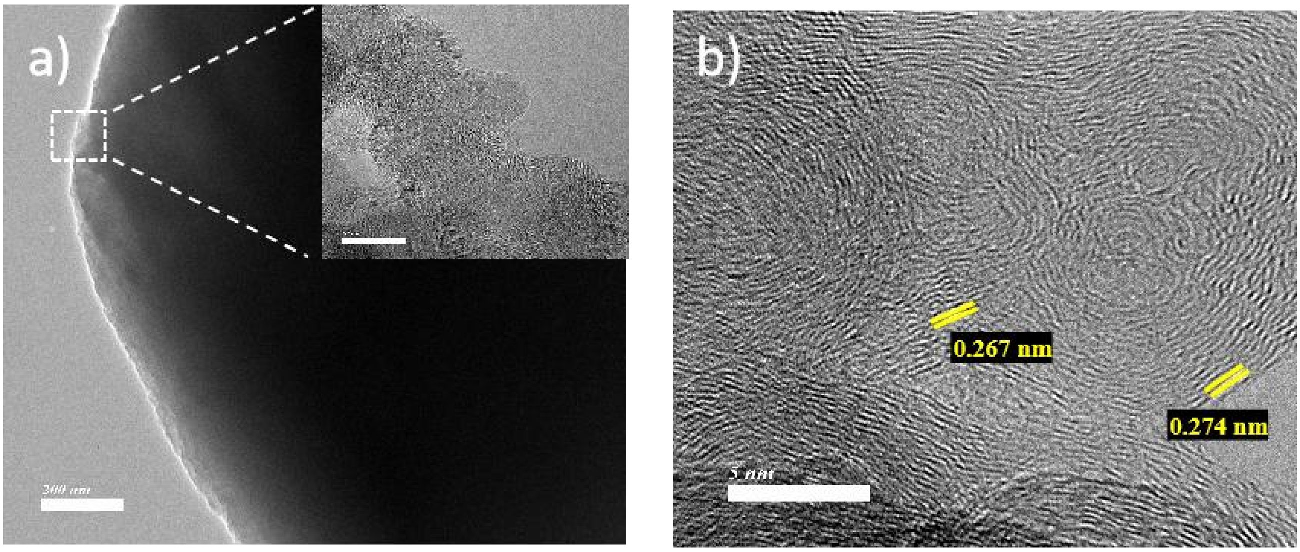


Figure 3.1 TEM image of hard carbon

3.1.2 TEM images of BPQDs

TEM images of black phosphorous quantum dots are shown in the figure 3.2. a) In the figure 3.2 a) Black Phosphorous quantum dots are evenly spread out and clearly visible which are distributed over a large area of 50 nm magnification. b) Crystal structure of the quantum dots is clearly visible. At the magnification of 5 nm. c) The interlayer spacing (d spacing) of Black Phosphorous quantum dots is around 0.164 nm

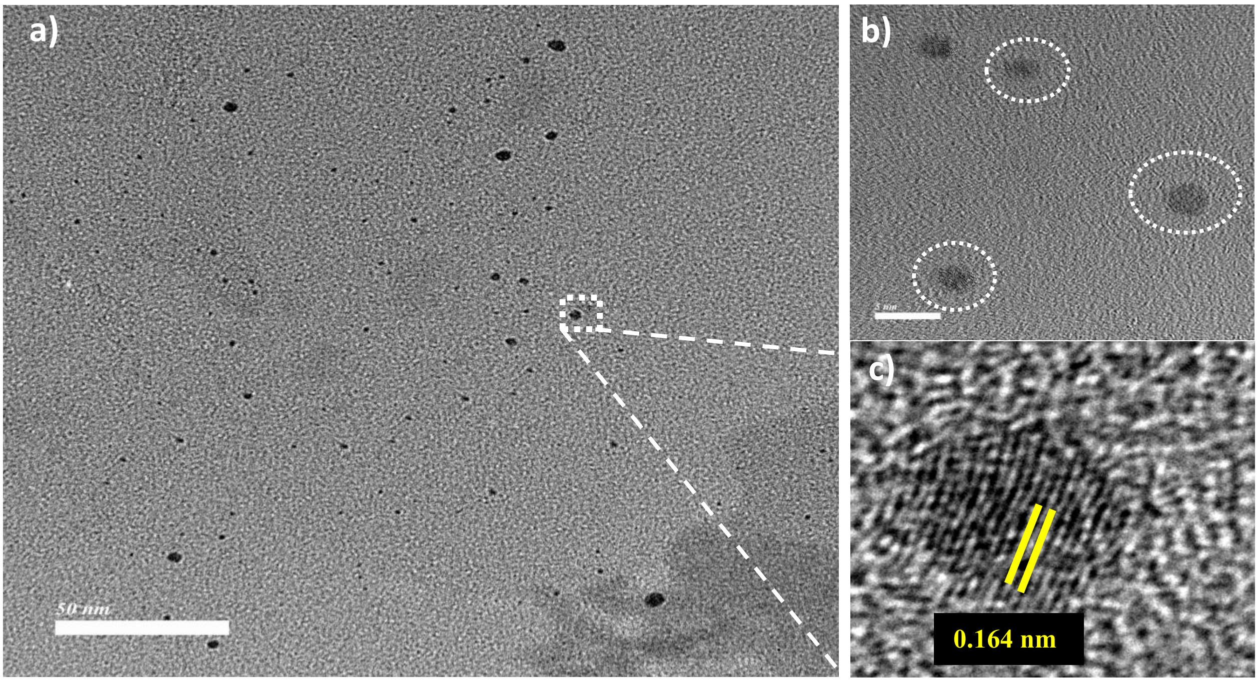


Figure 3.2 TEM image of black phosphorous quantum dots

3.1.3 TEM images of HC@BPQDs

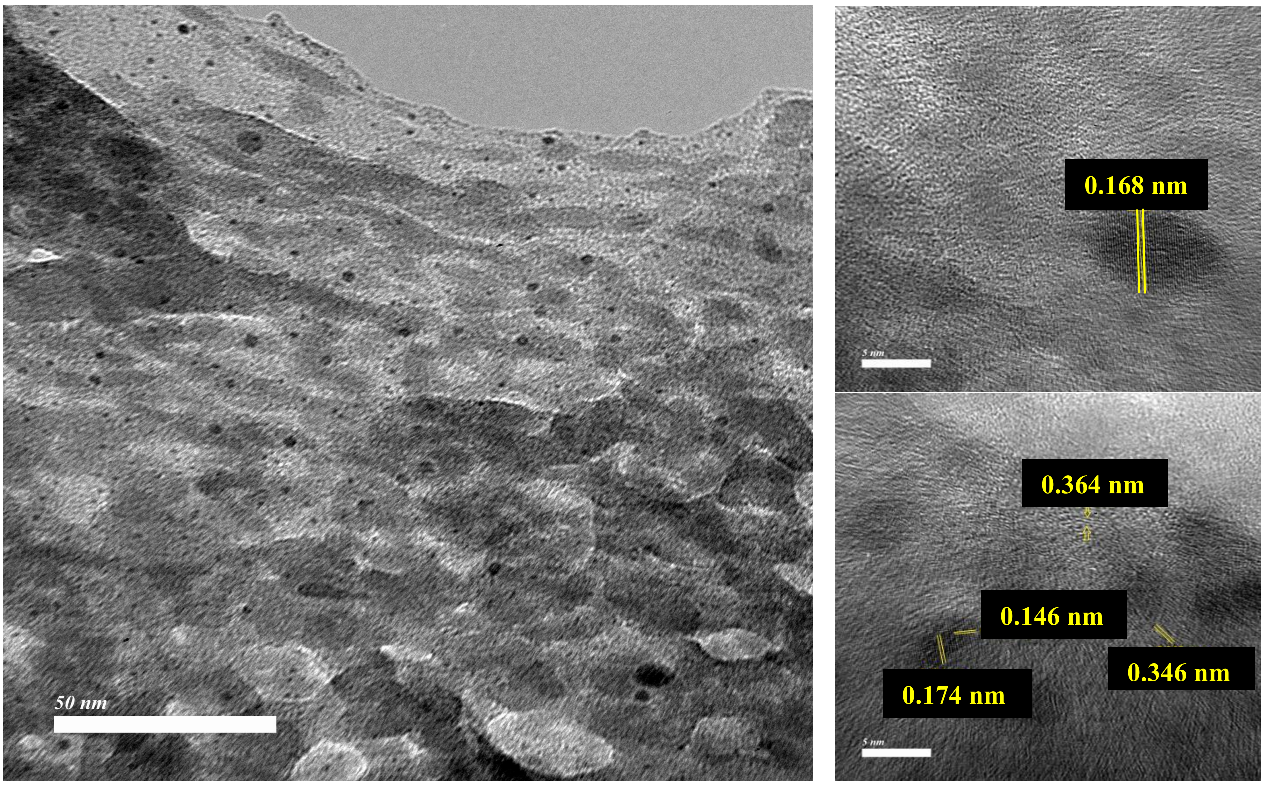


Figure 3.3 TEM image of HC@BPQDs

We incorporated the BPQDs in the hard carbon by infiltration method. In the figure 3.3 a) Black phosphorous quantum dots are evenly distributed over the hard carbon. b) Interlayer spacing of BPQDs situated on the hard carbon. c) Interlayer spacing of hard carbon and BPQDs on a surface of HC@BPQDs

These images give the solid proof that BPQDs are nicely distributed over the HC by the process of incorporation in the hard carbon with the help of infiltration method.

3.2 Field Emission Scanning Electron Microscopy (FESEM)

3.2.1 FESEM of hard carbon

FESEM analysis provides important insights into the morphology and structural properties of hard carbon, which directly influence its electrochemical performance in sodium-ion batteries. A well-optimized porous structure with randomly oriented particle distribution enhances charge storage, improves rate performance, and ensures long-term stability in battery applications.

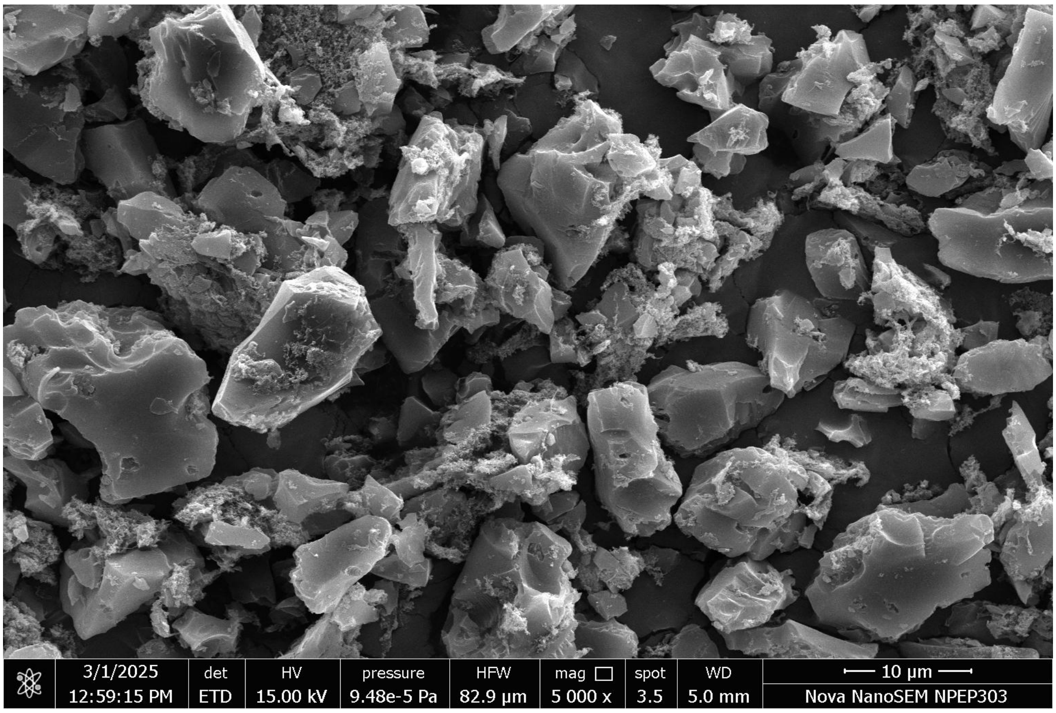
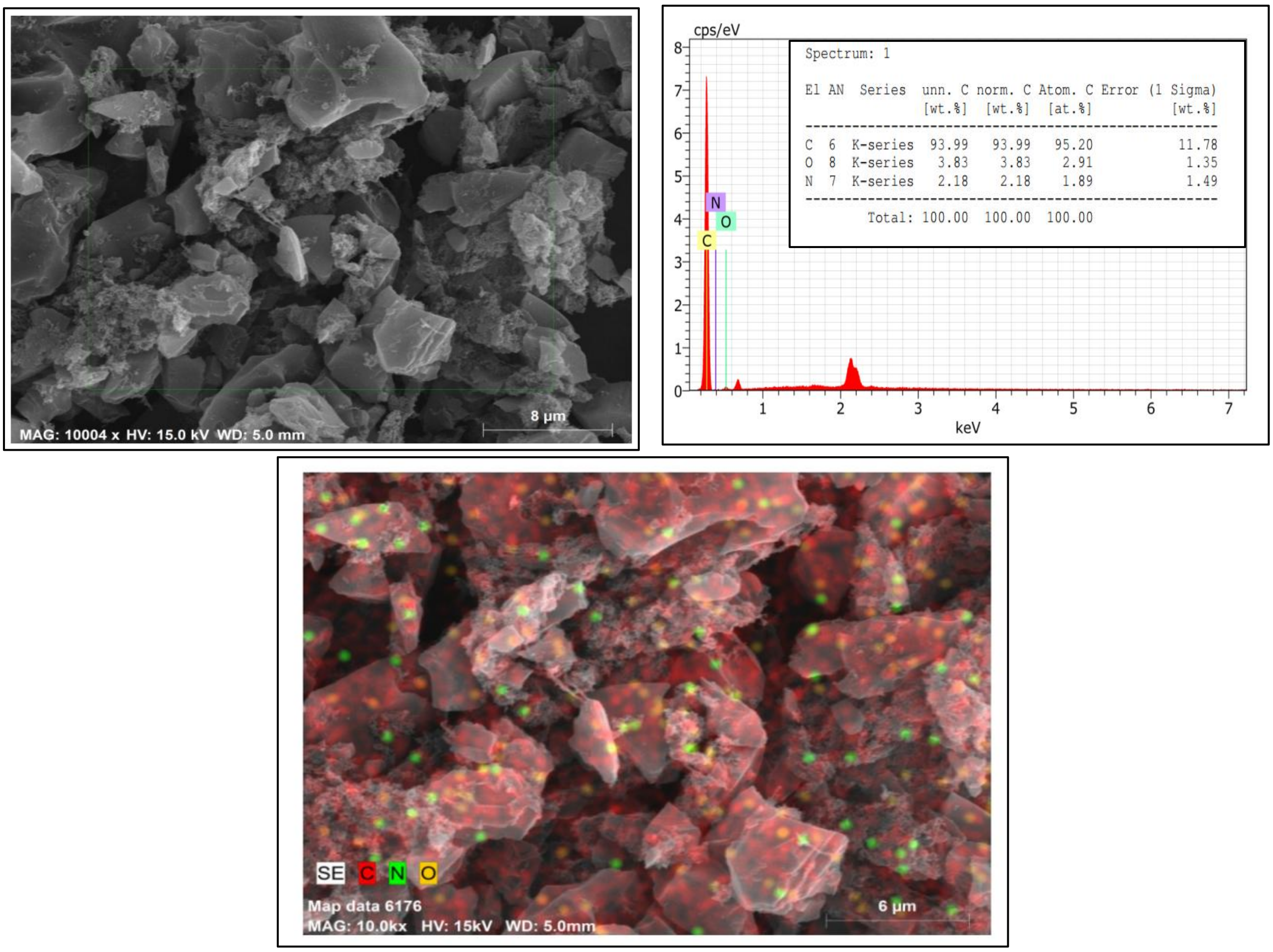


Figure 3.4 FESEM image of hard carbon

3.3 Energy Dispersive Spectroscopy (EDS)

3.3.1 EDS of hard carbon

Energy Dispersive Spectroscopy (EDS) is a widely employed analytical technique for determining the elemental composition of hard carbon. Typically, the EDS spectrum of hard carbon exhibits a prominent carbon (C) peak around 0.27 keV (figure 3.5), verifying its primary composition. Additionally, oxygen (O) and nitrogen (N) peaks may be detected, which are commonly attributed to surface oxidation or functional groups. Hard carbon samples are analyzed with a gold coating when prepared on conductive substrates. Maintaining high carbon purity is essential, as it enhances electrical conductivity and improves the electrochemical performance of sodium-ion batteries. By detecting impurities, EDS helps in refining synthesis parameters to optimize material quality. EDS is an essential technique for verifying the structural composition and purity of hard carbon.



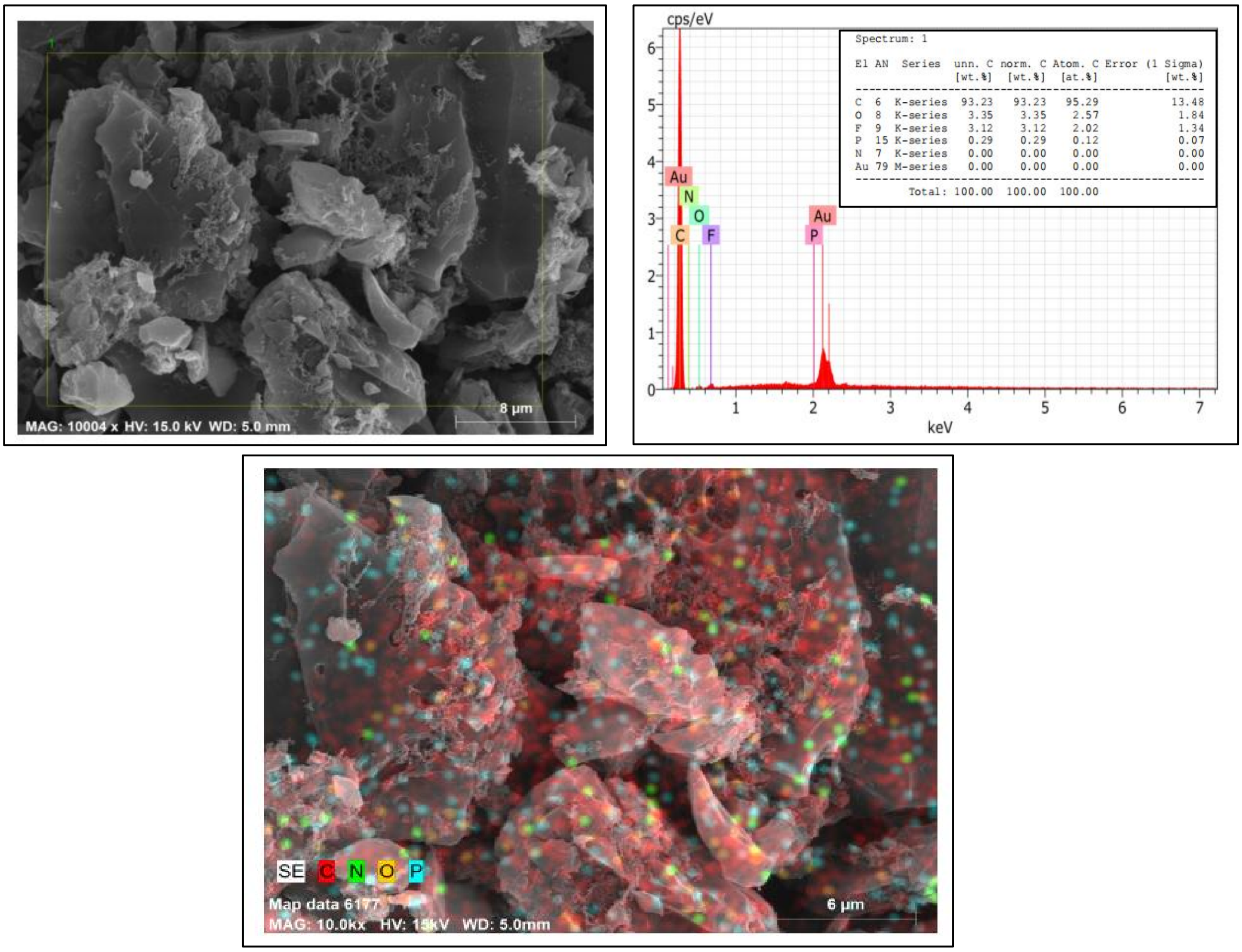
```
Spectrum: 1

El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]          [wt.%]
-------------------------------------------------------
C  6  K-series  93.99   93.99   95.20            11.78
O  8  K-series   3.83    3.83    2.91             1.35
N  7  K-series   2.18    2.18    1.89             1.49
-------------------------------------------------------
        Total: 100.00  100.00  100.00
```

Figure 3.5 EDS analysis of hard carbon

3.3.2 EDS of modified hard carbon (HC@BPQDs)

Figure 3.6 shows the EDS of modified hard carbon with BPQDs (HC@BPQDs). The peak of phosphorous gives the evidence of presence of phosphorous in the hard carbon. There are some other peaks present like Au, F, N, O. Au is from the substrate, F came from the PVDF binder and O and N shows surface impurities.

We can see in the following image that around 0.12 wt.% phosphorous is present in the give area having magnification is 8 micrometers. It shows that, throughout the sample there is a significant amount of BPQDs would be present to alter the properties of HC.



```
Spectrum: 1

El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]            [wt.%]
-------------------------------------------------------
C  6  K-series  93.23   93.23   95.29             13.48
O  8  K-series   3.35    3.35    2.57              1.84
F  9  K-series   3.12    3.12    2.02              1.34
P  15 K-series   0.29    0.29    0.12              0.07
N  7  K-series   0.00    0.00    0.00              0.00
Au 79 M-series   0.00    0.00    0.00              0.00
-------------------------------------------------------
         Total: 100.00  100.00  100.00
```

Figure 3.6 EDS analysis of modified hard carbon (HC@BPQDs)

3.4 PXRD of Hard carbon and Graphite

To make the differentiation between HC and graphite we did PXRD characterization.
PXRD data shows the amorphous nature, crystalline nature, planes associated and interlayer spacing values. Here we made observation from 5 degrees to 80 degrees by slow scan rate.

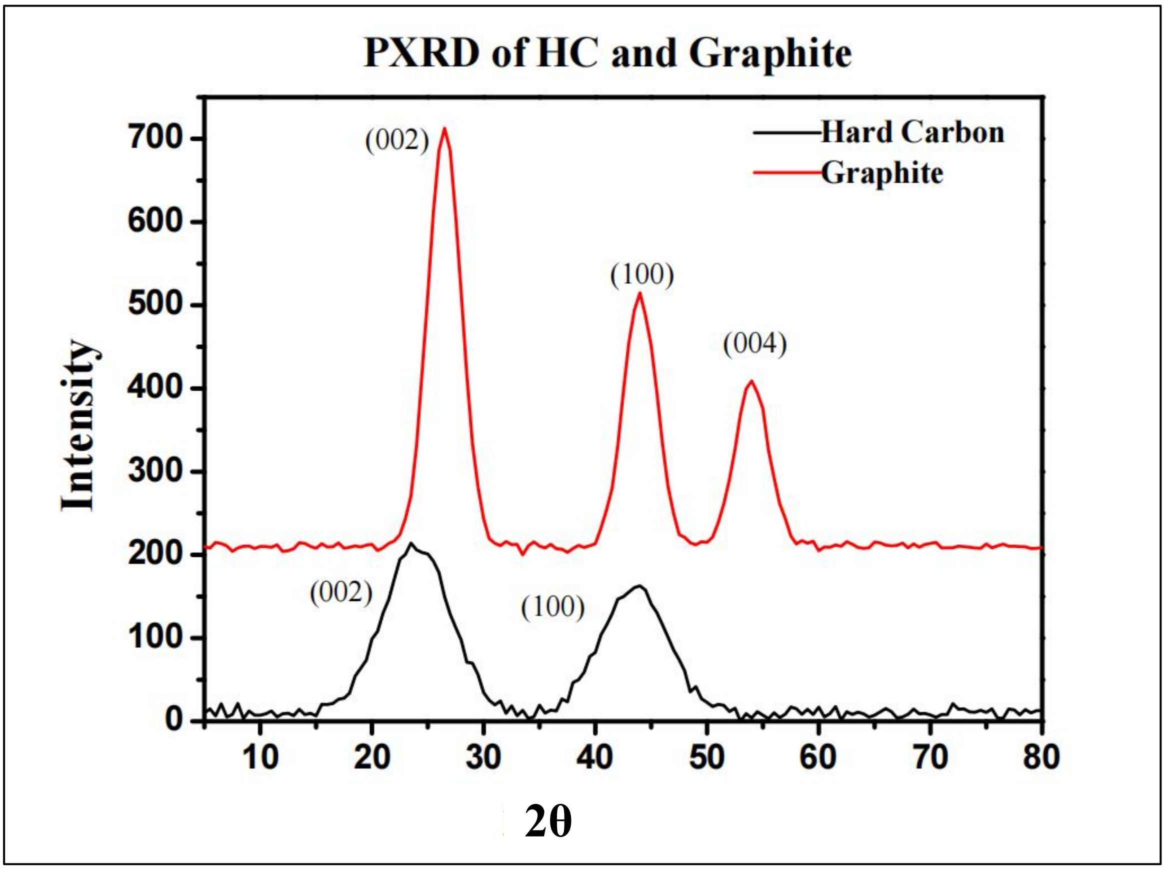


Figure 3.7 PXRD analysis of hard carbon and graphite

3.5 Electrochemical analysis

3.5.1 C-Rate capabilities

In this study cells are tested at different current rate to verify the performance of cell. In our study we applied gradual current like 25mA, 50mA, 100mA, 150mA, 200mA. Set the program for 5 cycle for each current till 200mA for both the cell shown in the fig 3.7.

3.5.2 Cycling Analysis

Here we set the both cell at 200mA current for cycling for 500 cycle and later increase the current to 500 mA. Cycling study gives idea about the stability of cell, capacity fading and longevity of cell at a particular current rate. Fig 3.8 shows the cycling data of both cells at 200 mA and 500 mA current rate

3.5.3 Impedance Analysis

We calculated the impedance for the both electrode. Impedance of a battery cell is a crucial parameter that provides insights into its internal resistance, reaction kinetics, and overall health. It is measured using electrochemical Impedance Spectroscopy (EIS), which applies an AC signal of varying frequency and records the response. Battery impedance consists of ohmic resistance, charge transfer resistance, and diffusion-related impedance.

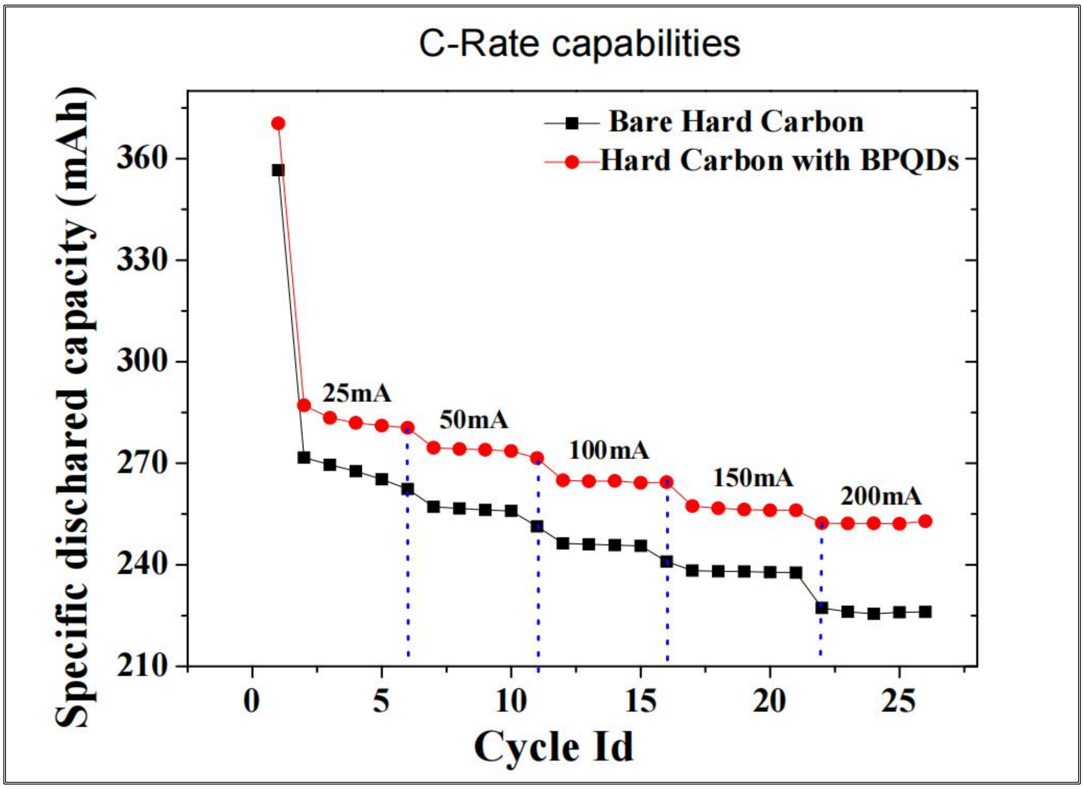


Figure 3.8 C- Rate capabilities of coin cell

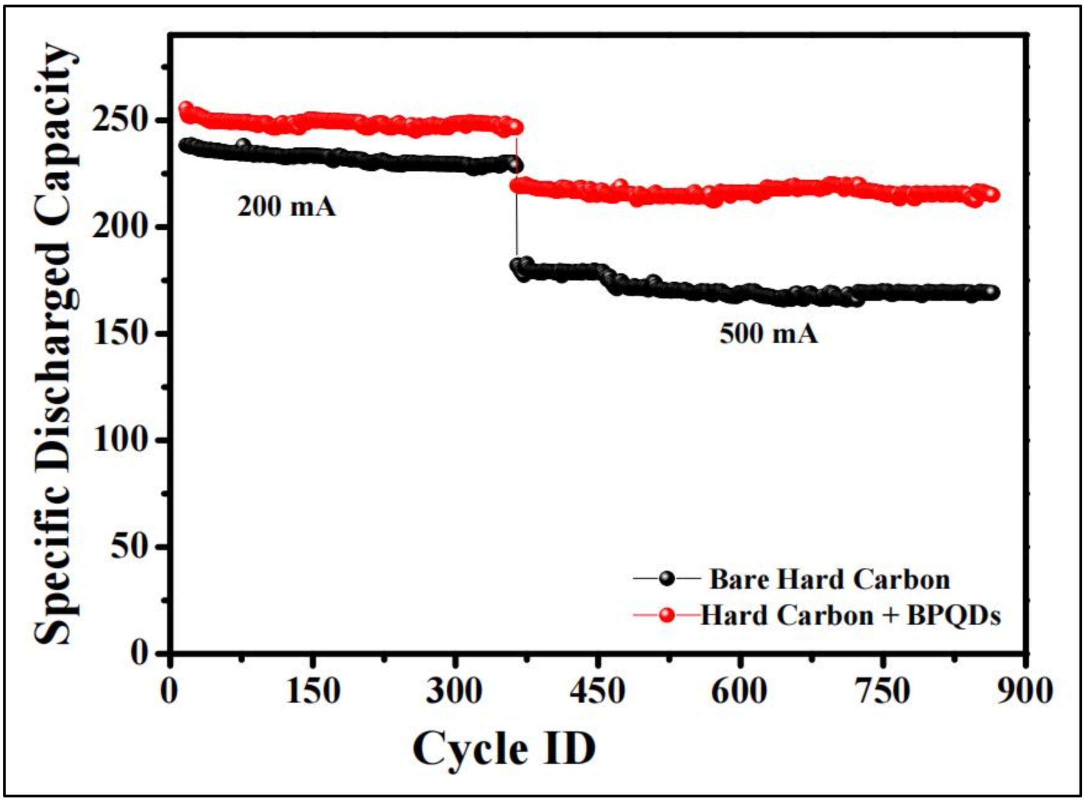


Figure 3.9 Cycling study of coin cell at different C-rate

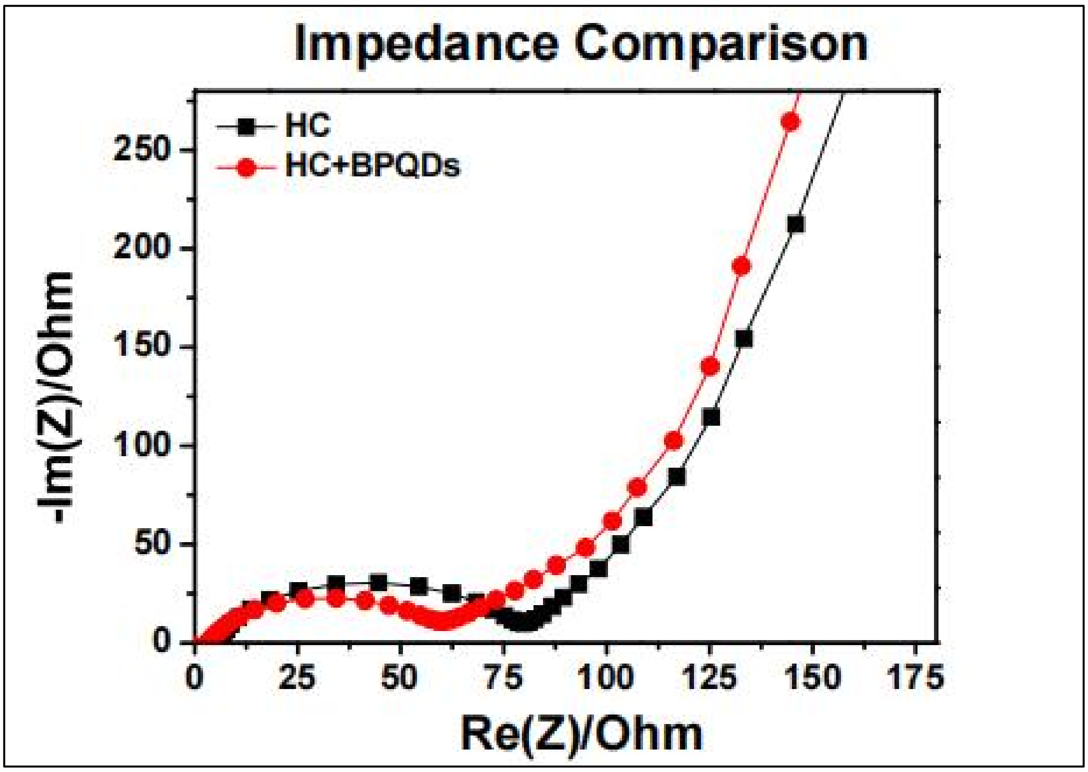


Figure 3.10 Impedance analysis of HC and HC@BPQDs

Chapter 4

Discussion

4.1 Discussion on HC@BPQDs

In the figure 3.3 the left-side TEM image shows a high-magnification view of BPQDs dispersed over the hard carbon surface. The dark contrast regions indicate the presence of BPQDs, which appear well-distributed and situated on the hard carbon matrix. The relatively uniform dispersion of BPQDs suggests effective interaction with the carbon surface, which is crucial for improving electronic conductivity and ion diffusion in sodium-ion battery applications.

The measured interplanar spacing (d-spacing) of 0.168 nm, 0.146 nm, 0.174 nm, 0.346 nm, and 0.364 nm correspond to different crystallographic planes of black phosphorus and graphitic carbon. The presence of 0.346 nm and 0.364 nm d-spacing indicate the (002) and (040) planes of black phosphorus, confirming the crystalline nature of BPQDs. The lattice fringes observed at 0.168 nm and 0.146 nm are associated with graphitic carbon, suggesting that hard carbon retains some degree of graphitization, which enhances electronic conductivity. The coexistence of black phosphorus and carbon lattice fringes confirms a strong interfacial interaction, which is beneficial for electron and sodium-ion transport.

The strong interface between BPQDs and hard carbon promotes faster electron transfer, reducing internal resistance which enhance the conductivity. The unique 2D structure of BPQDs introduces additional active sites for Na-ion adsorption, improving capacity retention. The well-dispersed BPQDs prevent excessive volume expansion during cycling, enhancing electrode longevity by providing structural stability.

4.2 Discussion on electrochemical performance

C-Rate Performance Analysis

The left graph evaluates the rate capability of both materials at increasing current densities (25 mA, 50 mA, 100 mA, 150 mA, and 200 mA). The specific discharged capacity is plotted against the cycle ID (Fig 3.8). The BPQDs-modified hard carbon (red circles) exhibits a significantly higher specific capacity than bare hard carbon (black circles) across all C-rates. At low current density (25 mA), the BPQD-modified electrode delivers an initial capacity exceeding 360 mAh/g, whereas bare hard carbon starts at a lower value. As the current increases to 200 mA, both electrodes exhibit capacity fading. However, the BPQD-modified electrode maintains a higher capacity (~260 mAh/g) compared to bare hard carbon (~230 mAh/g). The rate performance of BPQD-modified hard carbon enhanced. Improvement seen in the electronic conductivity due to BPQDs' unique properties. BPQDs modified electrode shows enhanced sodium-ion diffusion kinetics facilitated by additional active sites. The presence of a porous structure, which allows better electrolyte penetration and reduces charge transfer resistance.

Cycling Stability Analysis

The graph shows the cycling stability of both electrodes at two different current densities (200 mA and 500 mA) over an extended period (>800 cycles) (Fig 3.9). At 200 mA, the BPQDs modified electrode maintains a higher and more stable capacity (~250 mAh/g), whereas bare hard carbon stabilizes at a lower value (~230 mAh/g). Upon switching to 500 mA, a noticeable drop in capacity is observed in both materials. However, the BPQDs modified hard carbon retains a higher capacity (~230 mAh/g), while the bare hard carbon electrode drops below 190 mAh/g. This difference suggests that the incorporation of BPQDs enhances the structural stability of hard carbon, preventing severe capacity degradation over prolonged cycling. The better cycling performance of BPQDs modified hard carbon is due to Reduced irreversible capacity loss, Enhanced mechanical integrity, Stable solid electrolyte interphase (SEI).

These findings demonstrate that BPQD-modified hard carbon offers enhanced rate capability and cycling stability compared to unmodified hard carbon. The incorporation of BPQDs facilitates sodium-ion transport, minimizes polarization, and enhances long-term electrochemical stability, establishing it as a promising anode material for next-generation sodium-ion batteries.

Impedance Analysis

The Nyquist plot demonstrates that the modified electrode (HC + BPQDs) has a lower impedance than the unmodified HC electrode (Fig 3.10). This is evident from the smaller semicircle observed in the high-to-mid frequency range, signifying a reduced charge transfer resistance (R_{ch}). The incorporation of BPQDs appears to enhance electronic conductivity and facilitate charge transport by optimizing the electrode-electrolyte interface. Moreover, the Warburg tail in the low-frequency region is less prominent, suggesting improved ion diffusion and decreased diffusion resistance.

The decreased in impedance implies that BPQDs promote faster electrochemical kinetics, potentially by altering the solid electrolyte interphase (SEI) layer or increasing the available surface area for charge transfer. An improved SEI layer formation with BPQDs could enhance cycling stability and minimize resistance buildup over extended use. The superior conductivity and ion transport characteristics may also lead to improved rate capability and power output in battery applications. These results suggest that BPQDs are a promising additive for modifying the electrochemical behavior of HC electrodes, enhancing their suitability for high-performance energy storage systems.

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