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Applications of Recovered Valuable Metals and Nonmetals from E-Waste

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Abstract

This thesis presents an innovative approach to recycling spent anode graphite from discarded lithium-ion batteries, emphasizing the enhancement of electrochemical performance through asphalt coating. The research addresses the critical need for sustainable graphite resource utilization and environmental protection. The study introduces a novel asphalt coating method applied to purified spent graphite(PG) after impurity removal. The asphalt-coated purified graphite (ACPG) is thoroughly characterized using XRD, SEM,FTIR,EDS analyses, confirming successful coating and improved surface morphology conducive to electrolyte infiltration2.

The electrochemical performance of ACPG with varying asphalt coating amounts is meticulously investigated. The findings reveal that a 20% asphalt coating amount yields optimal electrochemical performance, with an initial capacity of 335 mAh/g at a 0.1 C rate, surpassing that of uncoated purified graphite (PG) Additionally, the rate capability is significantly enhanced post-asphalt coating, demonstrating the method's efficacy. The process also shows that the charge transfer resistance is also low in coated graphite compared to uncoated recycled graphite.

The thesis underscores the asphalt coating method's simplicity, effectiveness, and economic viability, offering promising prospects for industrial-scale processing of recycled graphite. The research contributes to the body of knowledge in lithium-ion battery recycling and presents a scalable solution to a pressing environmental challenge and reuses it in as a anode in LiB for further use.

Chapter 1 Introduction

1.1 WORKING OF LITHUM ION BATTERY:

A battery is made up of an anode, cathode, separator, electrolyte, and two current collectors (positive and negative). The anode and cathode store the lithium. The electrolyte carries positively charged lithium ions from the anode to the cathode and vice versa through the separator. The movement of the lithium ions creates free electrons in the anode which creates a charge at the positive current collector. The electrical current then flows from the current collector through a device being powered (cell phone, computer, etc.) to the negative current collector. The separator blocks the flow of electrons inside the battery. While the battery is discharging and providing an electric current, the anode releases lithium ions to thecathode, generating a flow of electrons from one side to the other. When plugging in the device, the opposite happens: Lithium ions are released by the cathode and received by the anode as shown in fig 1.1,1.2.

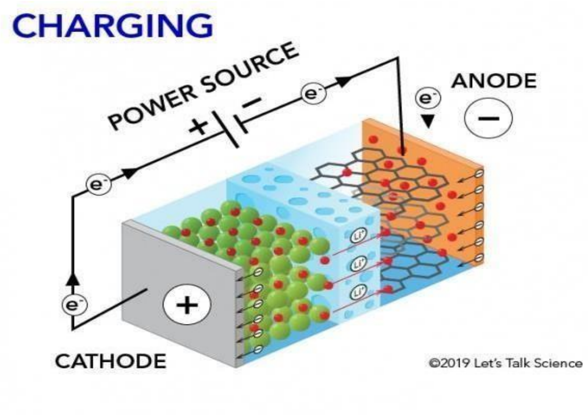


Figure 1.1: Charging Of Battery

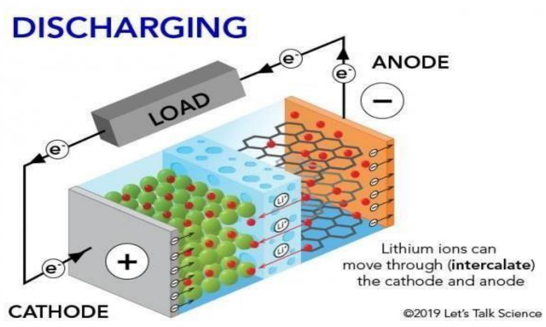


Figure 1.1:Dis Charging Of Battery

+Lithium-ion battery refers to a rechargeable high-energy battery in which Li is inserted and escaped from the positive and negative electrodes. The positive electrode generally uses lithium intercalation compounds, such as LiCoO ,LiNiO , LiMn O , etc., the negative electrode uses lithium-carbon 2 intercalationcompound Li C , and the electrolyte is an organic solvent in which lithium salts (such as LiP6F , LIAsF4 , LiClO , etc.) are dissolved. Solvents mainly include.(ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC) and chlorocarbonate (CMC). During the charging process, Li+ is Deintercalated back and forth between the two electrodes, which is vividly called "rocking chair batteries" (rocking chair batteries, abbreviated as RCB), as shown in Figure.

The chemical expression of lithium ion battery is first of all it form a stable compound with the alkali ions .The state-of-the-art LIB is mostly based ongraphite anode and a cathode family, including LiCoO2 (LCO), LiFePO4 (LFP), LiMn2O4 (LMO), LiNi1-y-zCoyMnzO2 (NMC), and LiNi1-y-zCoyAlzO2 (NCA) Li-GIC be a good substrate for reversible plating of extra Li, resulting in improved energy density of LIB. It provides high density of electric energy. So the process, spent graphite electrodes are recycled, leading to both environmental benefits and can be reused as a anode in LIB after asphalt coating Here are the key aspects of this groundbreaking approach:

1.2 RECYCLING PROCESS:

Sulfuric Acid Curing: The spent graphite electrodes undergo a curing process Using sfacid. This step prepares the material for subsequent**.**

Leaching: The cured graphite is leached to selectively remove impurities and Contaminants.

High-Temperature Calcination: The purified graphite is subjected to high-Temperature calcination, resulting in the regeneration of high-quality graphite material.

1.3 ASPHALT COATING PROCESS:

Carbon Source: Asphalt serves as the coated carbon source.

Liquid Phase Impregnation: The purified graphite is impregnated with liquid asphalt.

High-Temperature Treatment: The impregnated material undergoes high-temperature treatment.

Asphalt Pyrolyzed Carbon Graphite Composites The resulting material consists of asphalt pyrolyzed carbon coating on the graphite core.

By recycling spent graphite, this method significantly reduces the environmental impact associated with graphite disposal. It aligns with the principles of circular economy and sustainable development, contributing to a greener energy industry.

Enhanced Purity and Performance: The regenerated graphite achieves an impressive purity level of 99.6%.

Electrochemical performance tests demonstrate that the reclaimed graphite exhibits properties comparable to commercially available materials.

1.4 STRUCTURE ANALYSIS:

XRD L: These techniques are used to study minor changes in the internal structure and surface defects before and after the recovery process of spent graphite.

Particle Size Distribution and BET Surface Area Tests: These tests provide insights into the physical properties of the carbon-coated graphite.

1.5 CHARACTARISTIC TECHNIQUE:

XRD (X-Ray Diffraction): Used to investigate structural variations.

TEM (Transmission Electron Microscopy): Provides detailed information about the material's microstructure.

SEM (Scanning Electron Microscopy): Examines surface morphology changes.

1.6 EXPACTED OUTCOME:

Improved Electrochemical Performance: High Initial Specific Capacity: ACPG delivers an initial specific capacity at 0.1C, surpassing purified PG and close to Commercial graphite. Excellent Columbic Efficiency: Initial columbic efficiency (ICE) is 95.5%.

1.7 INDUSTRIAL VIABILITY:

The entire process is energy-efficient and generates minimal waste.

It can be implemented using readily available equipment, making it feasible for large-scale adoption in battery manufacturing.

In summary, this innovative graphite recycling method not only addresses environmental concerns but also contributes to the efficient utilization of resources in the energy sector. As we strive for sustainable solutions, such advancementsplay a crucial role in shaping a cleaner and more responsible future. First of all it form a stable compound with the alkali ions .The state-of-the-art LIB is mostly based on graphite anode and a cathode family, including $LiCoO_2$ (LCO), $LiFePO_4$ (LFP), $LiMn_2O_4$ (LMO), $LiNi_{1-y-z}Co_yMn_zO_2$ (NMC), and $LiNi_{1-y-z}Co_yAl_zO_2$ (NCA) Li-GIC be a good substrate for reversible plating of extra Li, resulting in improved energy density of LIB. It provides high density of electric energy**.**

Chapter 2 Literature Review

Graphite Recycling: The article discusses the significance of recycling graphite from spent lithium-ion batteries, highlighting its role in addressing graphite resource shortages and environmental protection

Novel Recycling Method: It introduces a novel method combining sulfuric acid curing, leaching, and high-temperature calcination to regenerate spent graphite, achieving a purity of 99.6% and good electrochemical performance2**.**

Impurity Removal Efficiency: The study compares the efficiency of the proposed method with direct acid leaching, showing superior results in impurity removal and environmental friendliness.

XRD Analysis of Graphite: Recent advancements in X-ray diffraction (XRD) have been pivotal in analyzing the crystalline structure of graphite. Studies have employed both quantitative and semi-quantitative phase analysis methods to determine the degree of graphitization and the ratio of 2H to 3R phase1. This is crucial for understanding the material's electrical and thermal conductivity, as well as its mechanical properties.

Performance of Graphite: Graphite's electrochemical performance has been extensively studied, particularly in the context of energy storage applications. The fabrication and characterization of graphite and graphene paste electrodes, with varying lateral flake sizes, have shown a clear correlation between flake size and electrochemical activity2. This relationship is essential .The regenerated graphite exhibits promising charge capacity and cycle performance, suggesting its potential for reuse in lithium-ion batteries.

Industrial Prospects: The study suggests that the asphalt coating method has potential for industrial-scale processing of recycled graphite, offering a sustainable solution for spent graphite utilization.

2.2 GAP IN LITERATURE

Recycling Efficiency: While the page discusses the improvement of electrochemical performance of spent graphite through asphalt coating, it does not address the overall efficiency and scalability of the recycling process1.

Environmental Impact: The document lacks a detailed analysis of the environmental impact of the asphalt coating process used in recyclingspent graphite.

Cost Analysis: There is no comprehensive cost-benefit analysis compar-ing the asphalt coating method to other recycling methods.

Performance Comparison: The page does not compare the performance of asphalt-coated spent graphite with new graphite or other recycle ed materials. These gaps could form the b asis of research questions or objectives for further investigation in your thesis. Remember to review the latest literature to ensure these gaps are still unaddressed.

Environmental Impact: The document lacks a detailed analysis the environmental impact of the asphalt coating process used in recycling spent graphite.

Chapter 3

Methods And Methodology

3.1. ELECTRICHEMOICAL DISCHARGE:

The residual voltage of a battery refers to the remaining voltage across its terminals after it has been discharged. It's an important parameter because it affects the overall capacity and performance of the battery. In the context of lithium-ion batteries (LIBs), the residual voltage can be influenced by various factors, including the state of charge, internal resistance, and the specific chemistry of the battery. It can cause the fire and blasting off battery if 2 electrode contact with each other during the dismantling of battery, so the battery residue voltage should be nil and can be done by discharging

Electro chemical discharge is electrolytic discharge or salt-solution immersion discharge, also known as electrochemical discharge in a conducting solution but it is not environmental friendly as it contaminates the solution. As the concentration of the salt increase the rate of discharge of residue voltage increases thus we can say the discharge efficiency increases. 250 mL of 1 mole/L, 0.5 mole/L, and 0.3 mole/L NaCl, Na_2SO_4, Na_2CO_3, and $MnSO_4$ solutions were prepared. Here we took the battery of Samsung 2500 mAh cell.

Re = The residual voltage /The initial voltage × 100%.

Making of 1M NaCl solution in water of 250 ml of mass 14.61gm nacl required. The making of solution is shown in fig 3.1,3.2

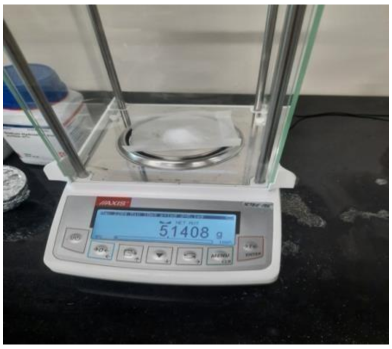


Figure 3.1: Measuring NaCl **Figure 3.2: Making of solution**

Then the battery is dissolve in the solution to discharge completely. It can be better done with the platinum electrode connected which doesn't contaminate the solution.

Figure3.3: Discharging of Battery in solution

The bubbles of chlorine gas comes out of anode from the battery in solution during discharging. it produces Na+ and Cl- ion. We know that ion is a charge carrier. Thus conductivity of water can be increased by adding salt. But when you apply voltage, the Na+ ion gets attracted by the cathode and Cl- ion combined with another ion at anode to from chlorine gas as shown in fig 3.3.

Then taking reading at different time of the battery to find out the residue voltage with the help of multimeter.

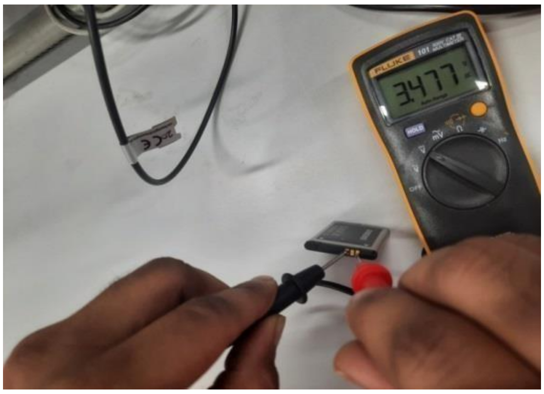


Figure 3.4: Measuring Residue volt

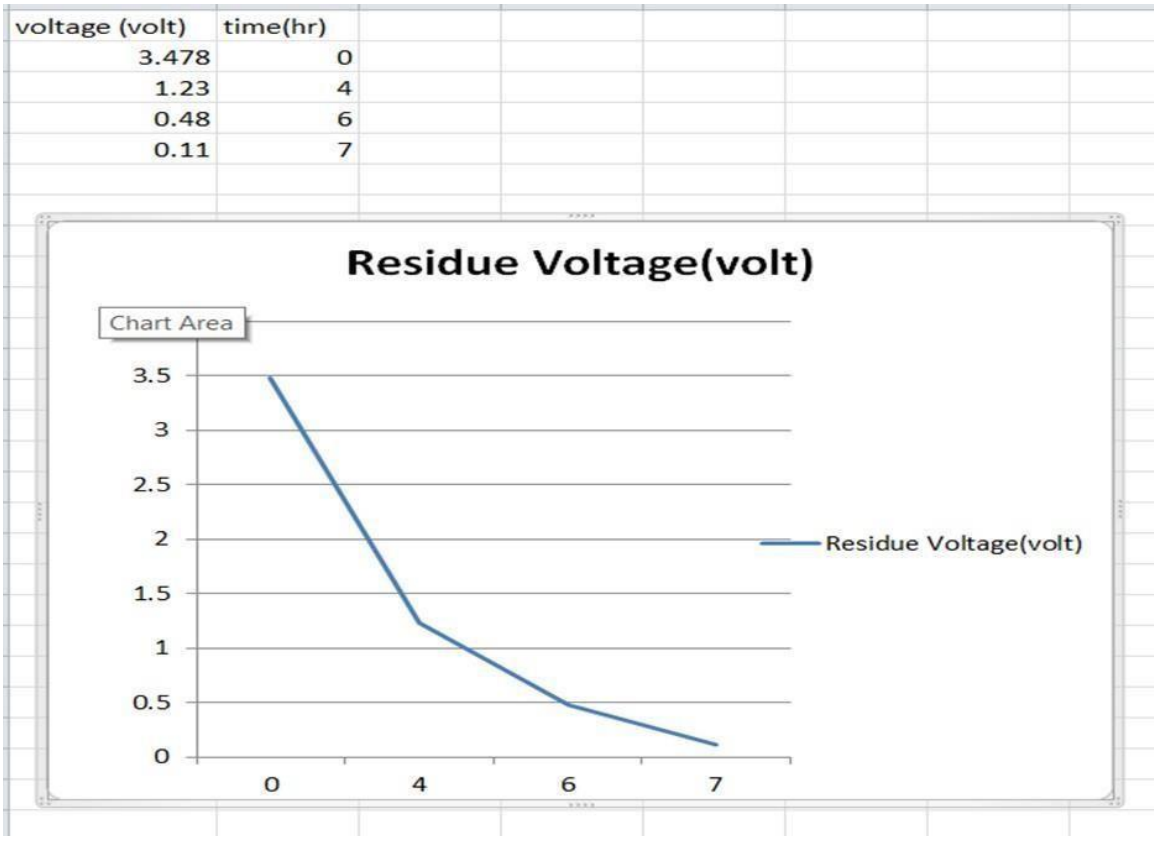


Figure 3.5: Graph of Residue voltage vs. Time

It shows residue voltage vs. time battery is ready 2to dismantle at 7 hrs.fig3.5 graph.

3.2 BATTERY DISMANTLING:

Separating the battery packs and modules into recyclable units, such as individual cells. The picture below shows the Anode Separator and Cathode of the dismantledbattery

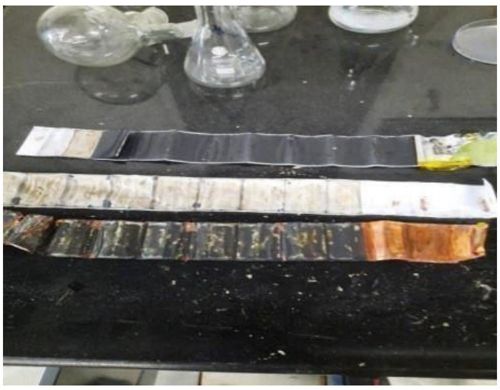


Figure 3.6: Dismantling Of battery

3.3 LEACHING & CURING:

This novel method combines sulfuric acid curing with leaching to regeneratespent graphite from lithium-ion batteries. It's more efficient than direct acid leaching, achieving a graphite purity of 99.6%.. The process effectively removes impurities such as Li, Co, and Fe from spent graphite. The sulfuric acid acts as an oxidant, transforming high-valence oxidesand metals into corresponding sulfates, which are then dissolved in a leachingsolution. In 250 ml of water in which 25% of it sulfuric acid will be added for making leaching solution to leach graphite from copper. Dip the anode leaching solution shown in fig 3.7.

Figure 3.7: Anode in leaching Solution

Now we put the anode in leaching solution and mix with magnetic pallet 400 rpmspeed shown in fig 3.8

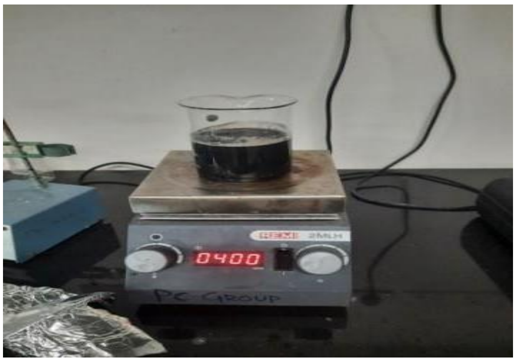


Figure 3.8: Mixing Of Solution

3.4 FILTRATION:

FILTRATION of impure graphite with filtration paper. To remove graphite with dissolve H_2SO_4 from the solution. Shown in fig 3.10

Figure 3.10: Filtration

3.5 CALCINATION:

Calcination, in simple words, can be described as a process of heating some solid material or a substance in a controlled environment. Usually, in the process, the temperature is also regulated. Calcination is done to bring about some change in the substance's physical or chemical constitution. During calcination, solids are heated at high temperatures. This is done to mainly remove volatile substances and water or oxidize the substance. This process is also known as the purification. The impure graphite is kept in the muffle furnace for 1 hour and extra 40 min for reaching the temperature of 1000 C and keeping out of it. Temperature Ramp is 20 C/min. The image shown below

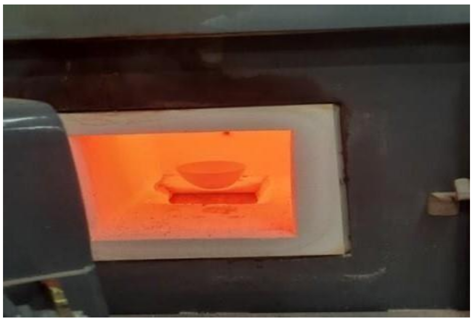


Figure 3.11: Calcination in Muffle Furnace

3.6 OUTCOME:

The mass Of purified graphite (PG)obtain is 2.8 gm. As shown in below fig 3.11. Mass loss is 0.3 gm. which is

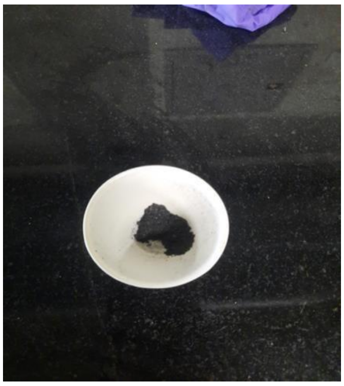


Figure3.11: Purified Graphite

due to calcination in muffle furnace.

Now we separated 1.4 gm. of purified graphite powder for making electrode for electrochemical test and 1.4 gm. asphalt coating process for enhancing electrochemical performance and reuse it.

3.7 ASPHALT COATING PROCESS:

Asphalt dissolved in tetrahydrofuran and stirred with magnetic pallet for 30 min shown in fig 3.12, 3.13.

Figure 3.12: Asphalt and THF

Figure 3.13: Dissolving Asphalt in THF

We use THF because of following reason,

- Polarity: THF is a polar solvent, which allows it to dissolve a wide range of polar and non-polar compounds.
- Miscibility with Water: THF is miscible with water, meaning it can mix in all proportions, which is useful in many chemical reactions
- Low Viscosity: Its low viscosity makes it easy to handle and mix with othersubstances

3.8 ULTRASONIFICATION:

A technique using sound waves to break down particles is a process that uses high-frequency sound waves to break down large particles into smaller fragments or uniform-sized particles in a fluid Ensure even distribution of asphalt particles in the coating solution. Improve the quality and uniformity of the asphalt coating on the graphite. Aiding chemical reactions necessary for the coating process. It took over 30 minutes as shown in fig 3.15.Filtration and adding of graphite powder in the solution then followed by againUltrasonification of 30 min.

Figure 3.15: Ultrasonification of Solution

3.9 ROASTING:

Roasting is a thermal treatment process where materials are heated to high temperatures in the presence of air or an inert atmosphere. In the context of asphalt coating for graphite, roasting serves several purposes: It helps in breaking down and removing organic binders and other impurities from the spent graphite also. High-temperature roasting can repair the structural damage in graphite, improving its Crystallinity and overall quality.: Roasting prepares the graphite surface for better adhesion of the asphalt coating, ensuring a uniform and effective coating layer. After coating, the mixture is roasted in a vacuum tube furnace at 110°C for 8 hrs. toremove impurities with argon gas to decompose the asphalt and form a conductive carbon layer on the graphite. shown in fig 3.16.

Figure 3.16: Tubular Furnace

3.10 OUTCOME:

Figure 3.17: asphalt Coated Graphite

3.11 CHARACTARIZATION:

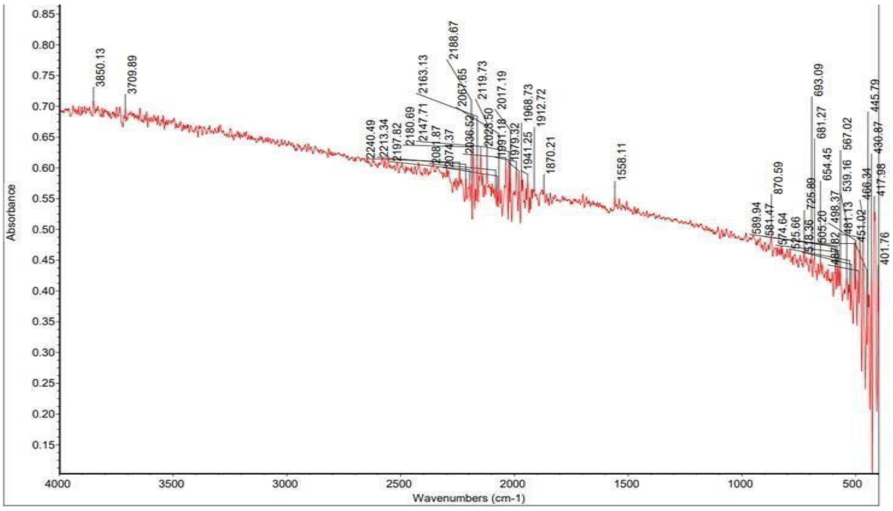
- XRD Analysis: Samples were analyzed using X-ray diffraction (Cu-kα radiation)over a range of 2θ between 10° and 90°.
- Microscopy: Morphology was observed using scanning electron microscopy(SEM)

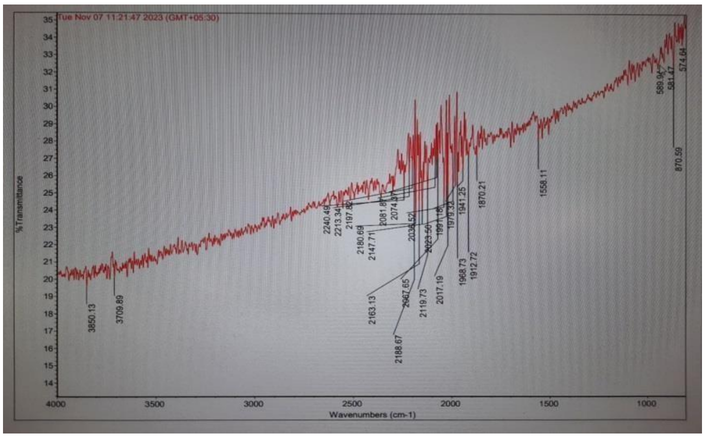
Size Distribution: It is observed by XRD data Impurities are observed by FTIR,EDS.

Chapter 4

Result and Discussion

4.1 SURFACE MORPHOLOGY AND IMPURITIES:





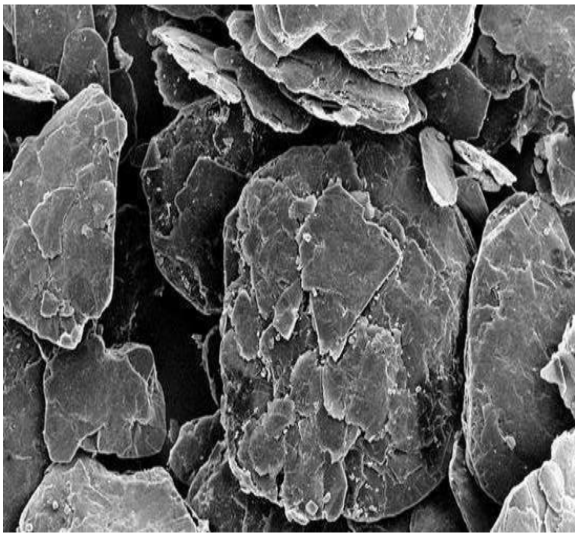


Figure 4.1: SEM of Spent Graphite

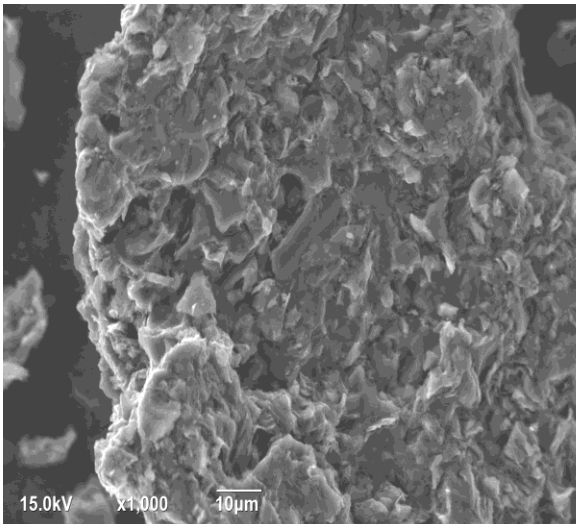


Figure 4.2: SEM of Purified Graphite

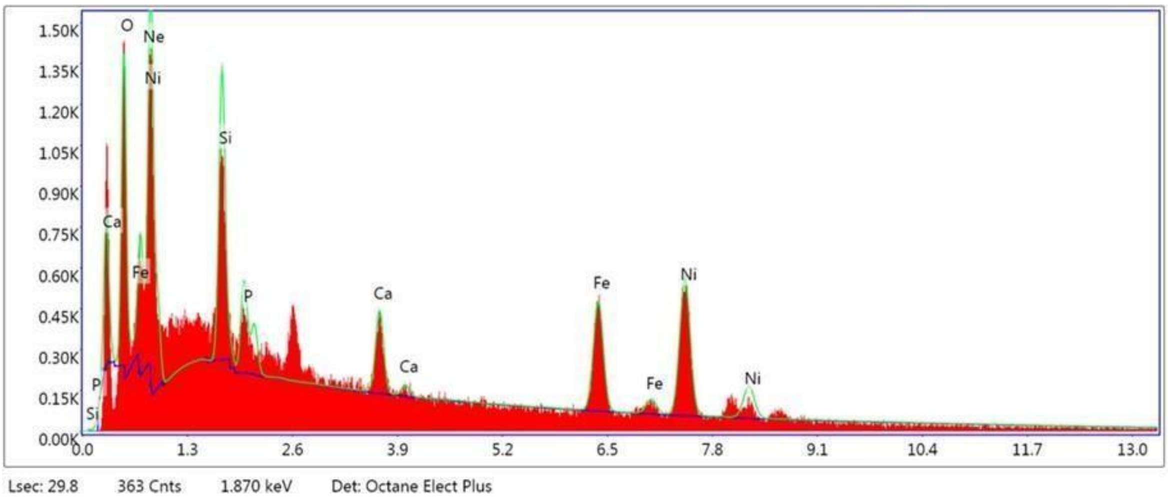
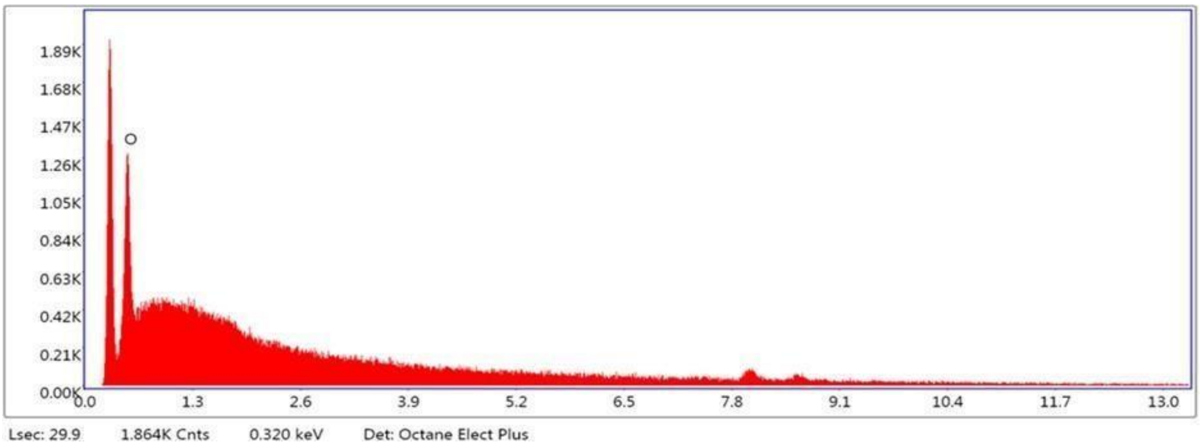


Figure 4.3: EDS Graph and Data of Spent Graphite for impurities

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
O K	14.07	32.23	301.53	5.75	0.0722	0.7636	0.6719	1.0000
NeK	0.00	0.00	0.03	99.99	0.0000	0.7263	0.5666	1.0000
SiK	12.21	15.94	343.85	4.67	0.0692	0.6951	0.8133	1.0026
P K	5.08	6.01	112.68	5.83	0.0287	0.6702	0.8387	1.0039
CaK	7.84	7.17	126.57	8.13	0.0537	0.6781	0.9866	1.0240
FeK	22.01	14.44	207.75	5.16	0.1532	0.6437	1.0053	1.0753
NiK	38.79	24.21	275.31	3.85	0.2617	0.6716	0.9969	1.0079



Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
O K	100.00	100.00	262.33	5.58	0.9107	0.7290	1.2492	1.0000

Figure 4.4: EDS Graph and Data of Purified Graphite for impurities

4.1.1 ANALYSIS OF IMPURITIESAND SURFACEMORPHOLOGY, FTIR of PG ,SG&ACPG:

Particle Size: SG particles are about 20−30 µm in size**.** After treatmentPG particle□becomes smaller, about 15−25 µm..

Surface Impurities: From fig4.3 4.4 SG has considerable white substance between particles, containing elements like Oxygen, Ferrous, Nickel, Cobalt,& Calcium and PG only have O, Li and binder and some water vapor which can be classified from FTIR. Lithium can't be detected because it is a light element so the energy of X-ray is less so it can’t be measure in EDS. These substances are residues from metal elements and decomposed electrolyte products.

Post-Treatment Changes: After sulfuric acid curing−leaching, the surface of PG is rough with some white substance remaining or charge deposition due to some nonconductive area.

Surface Texture: The surface of RG turns rough and regular, which isbeneficial for electrolyte infiltration and can potentially enhance electrochemical performance as analyzed from fig 4.1,4.2. This can reduce the SEI formation to some extent but roughness can increase charge transfer resistance in Electrolyte-Electrode Interface leading to poor electrochemical performance which not suitable for anode in LIB.

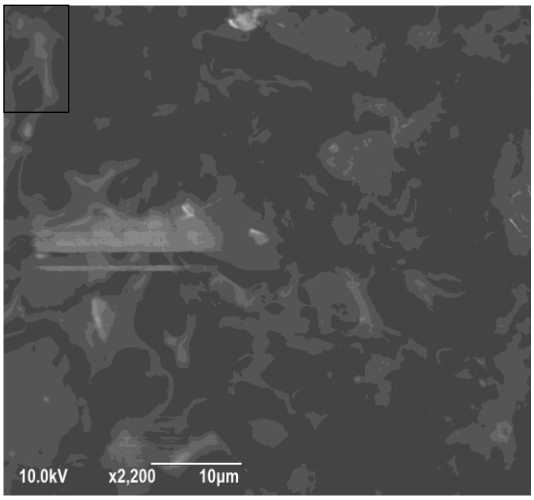


Figure 4.5: SEM of ACPG

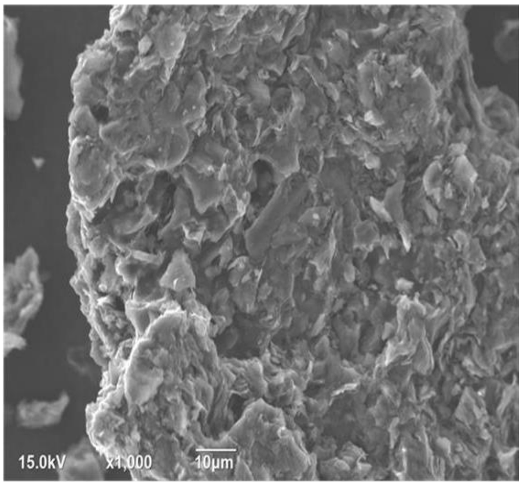
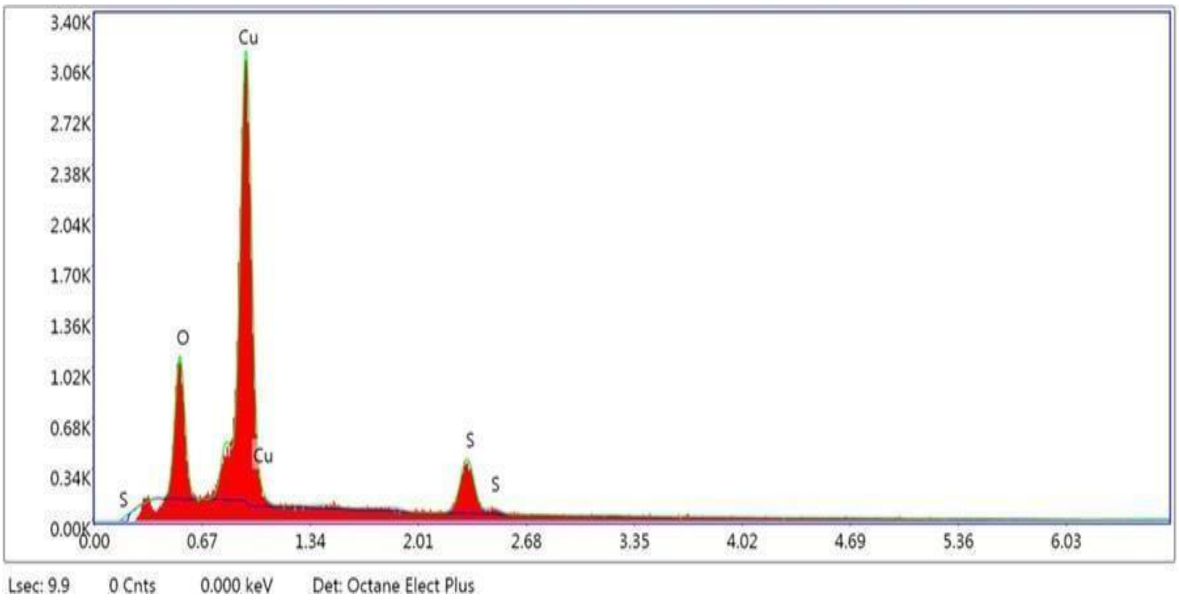


Figure 4.6: SEM of Purified Graphite



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Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
O K	12.15	32.50	760.85	4.85	0.0845	0.8100	0.8588	1.0000
CuL	75.26	50.69	2152.98	3.75	0.4868	0.5820	1.1113	1.0000
S K	12.59	16.81	394.93	5.42	0.0893	0.7359	0.9610	1.0031

Figure4.7: SEM of ACPG

4.1.2 ANALYSIS OF IMPURITIES AND SURFACEMORPHOLOGY OF ACPG:

From fig 4.5 and fig 4.6 we can say that:

Surface Texture: The surface of PG is described as coarse and uneven with step-like layers and holes while ACPG is with almost no holes or cracks**.** The smoother surface from increased asphalt content can reduce lithium consumption in the formation of the solid electrolyte interphase (SEI) film.

Reduced Scattering: A smoother surface minimizes scattering of charge carriers, allowing for more direct pathways and efficient transfer.

Decreased Defects: Smoothness implies fewer surface defects thatcan act as barriers or traps for charge carriers.

From EDS we can found the contents and impurities of asphalt that is coated the I mpurities or additional group are present in the sample are sulpher copper which may came from the Asphalt and oxygen and lithium which can be identified from EDS. This all things will help in increasing the electro-chemical performance of the graphite when reuse it as a anode in LIB.

4.2 STRUCTURAL ANALYSIS:

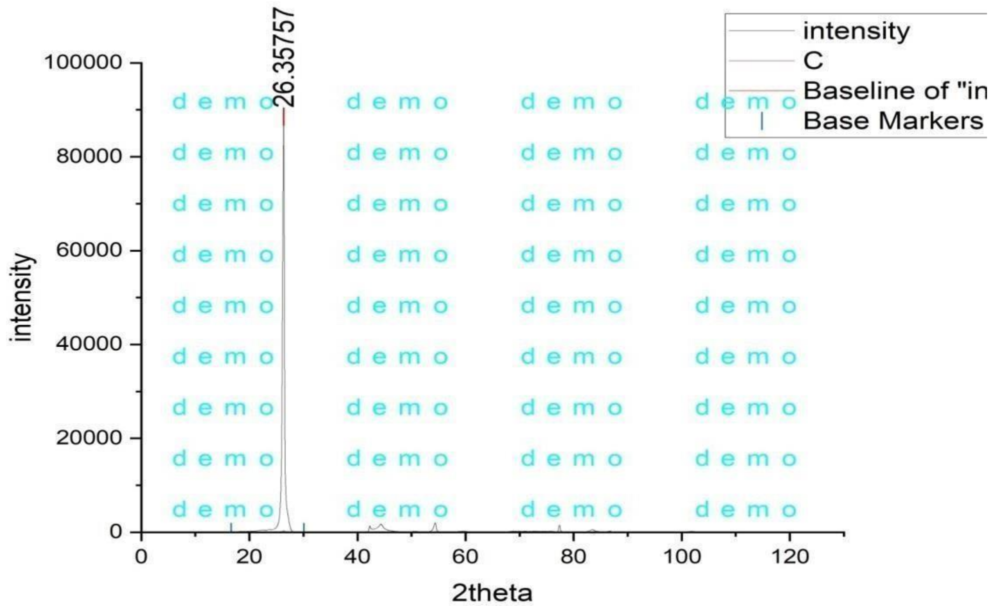


Figure 4.8: XRD Of Purified Graphite

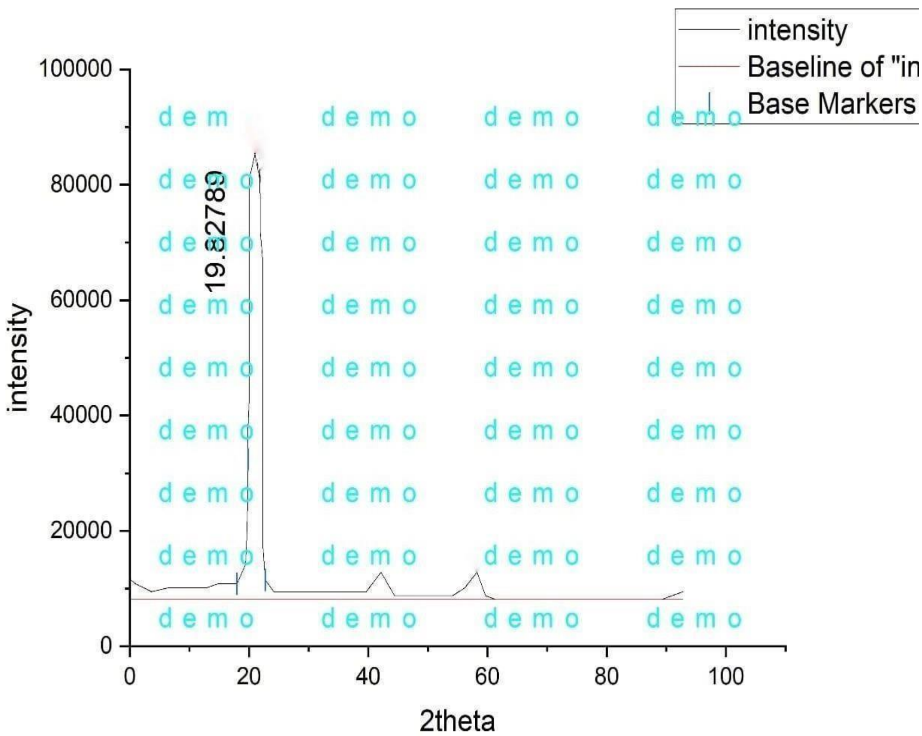


Figure 4.9: XRD Of Asphalt Coated Purified Graphite

Table 4.1: Properties & characteristics from XRD plot of Purified Graphite

wave length	2theta	theta	D-space(Å)	planer(h,k,l)	lattice	FWHM	Height	crystallitesize Å	MICROSTRAIN	lattice parame (ahex,chex) Å
1.54	26.35	13.175	3.378288	1,1,1	hexagon	0.40003 Å	8960	3.71	0.42	3.37,5.815

			8		al		2.58			
1.54	44.14	22.07	2.0492944	1,1,0						
1.54	54.43	27.215	1.6836829	2,2,2						

Table 4.2: Properties Characteristics from XRD of Asphalt Coated Purified

Wave length	2theta	Theta	D_SpACE	FWHM	height	Crystallitesize	Micro-Strain	Lattice parameter
1.54	19.82	9.91	4.474116	19.56233	83108.08	0.075120211	27.99293	4.47,7.74

From fig 4.8 and fig 4.9 we can conclude that ACPG shows a strong diffraction peak at 19.82°, indicating a crystalline hexagonal structure. Which is less than PG of 26° because Interplanar spacing increases The reason are as follows:

High-Temperature Repair: The process of high-temperature treatment during the regeneration of graphite anode leads to a reconstruction of the graphite structure.

This results in an increase in the interlayer lattice distance**.**

Degree of Graphitization: The modification with asphalt coating contributes to a higher degree of graphitization, which is associated with an increase in the interlayer spacing**.**

Particle Aggregation Reduction: Asphalt coating helps reduce the aggregation of graphite particles, which can contribute to a smoother surfacemorphology and potentially increase the interlayer distance.

The Crystallite sizes is also decreases due to amorphous nature (short range order) the size can be calculate from Scherrer equation **D= K λ / (FWHM * cosθ) .** Due to peak broadening and increase of FWHM (Full Width At Half Maximum) the crystallite size are as 3.71 and 0.071 of PG & ACPG respectively from the table

4.1 and 4.2.

The lattice parameter also changes after coating which is again due to may doping in the unit cell or lattice.The micro strain is also more in asphalt coated graphite due to maybe of the procedure thermal treatment A study on the high-temperature rheological properties of emulsified asphalt residues indicates that the mechanical properties ofthe residue, which include micro-morphology changes, have a significant impact on the performance of emulsified asphalt mixtures. This implies that the coating process, which involves emulsification and aging, can alter the rheological properties and micro-morphology of the asphalt, potentially affecting the micro strain of the coated material.The shift in peak can be also due to the impurities which is in the unit cell.

Table 4.3: Crystallinty calculation of ACPG &PG

peaks	area	2theta	overall area	crystalinity	percent
1	47335.13	26.35757	60326.787	0.8947189	89.47
2	713.7811	42.32157			

3	3685.546	44.32357			
4	1372.483	54.37257			
5	868.5739	83.45357			
Crystallinity of Asphalt Coated Purified graphite					
1	17723.25	19.82789	268433.33	0.7171818	71.17
2	138787.1	21.68675			
3	13676.36	42.13425			
4	22328.75	56.38555			

Crystallinity refers to the degree of structural order in a solid. In a crystal, atoms or molecules are arranged in a regular, periodic manner, which influences the material's properties like hardness, density, and transparency. It can be calculated from XRD by the formula given brelow figure

$$\%\text{Crystallinity} = \left(\frac{\text{Area under crystalline peaks}}{\text{Area under all peaks}}\right) \times 100$$

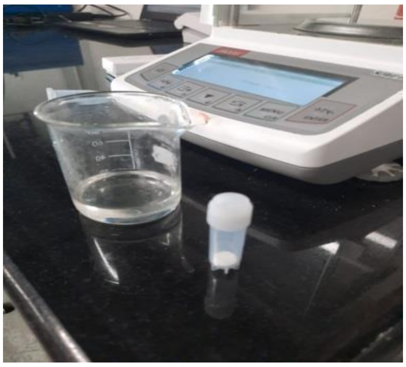
This shows correctly that the ACPG is less crystalline with 71.17% compared toPG with Crystal linty of 89.47% which is true which can be seen from table 4.3

4.3 ELECTROCHRMICAL PERFORMANCE:

4.3.1 Electrochemical Impedance Spectrometry:

Making of electrode and setup of workstation:

Charge (Li^+ intercalation)/discharge (Li^+ de-intercalation) measurements were performed in a CR 2016-type coin cell with two electrodes. Li metal foils were used as a counter electrode. The working electrode was preparedby mixing 93 wt.% active materials with 5 wt.% polyvinylidene fluoride (PVDF) in N-methylpyrrolidone (NMP). The slurries of the mixture were coated onto a copper foil current collector and then dried in a vacuum ovenat 110°C for 12 . The disks were weighed with an electronic analytical balance . The cell was assembled in a glove box where the concentration ofO_2 and H_2O was less than 0.1 ppm. The electrolyte solution was 1 M
$LiPF_6$ dissolved in ethylene carbonate (EC)/diethyl carbonate (DEC)/ethyl methyl carbonate (EMC) at 1:1:1 by volume. Electrochemical impedance spectroscopy (EIS) measurements were performed with an electrochemicalworking station at room temperature (25°C), and the EIS



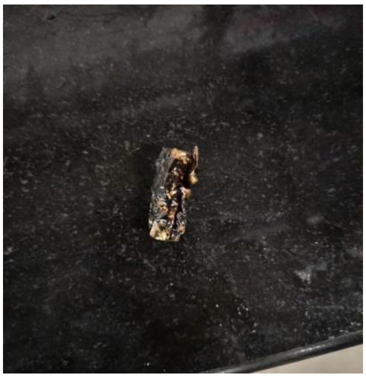


Figure 4.10 :Asphalt Coated Graphite Anode

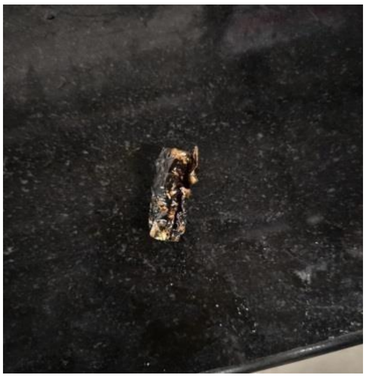


Figure 4.11 : PVDF and NMP

spectra were obtained in a frequency range from 0.01 Hz to 100 kHz. The image of electrode given below.

EIS A technique used to measure the impedance of a system over a range of frequencies. It's commonly used in battery research to analyze the electrochemicalproperties and performance of materials. Here we plot the nyquist plot means plotting the magnitude and phase of a transfer function or a system in a same complex plane .

Different Circuit elements of EIS

Charge transfer resistance: often denoted as Rct, is a key parameter in electrochemical impedance spectroscopy (EIS) that represents the resistance to the transfer of charge across the interface between an electrode and the electrolyte in an electrochemical cell. It is one of the components used to model the impedance of an electrochemical system and is associated with the kinetics of the faradaic (charge-transfer) reactions occurring at the electrode surface. The value of Rct can provide insights into the reaction rate and is influenced by factors such as the electrode material, surface area, and the concentration of reactive species. In EIS, Rct is typically represented in an equivalent circuit model and can be estimated from the diameter of a semicircle in a Nyquist plot, which is a graphical representation of theimpedance data. **Rct=(n2F2)/Ak0CRT** where (R) is the gas constant, (T) is the temperature, (n) is the number of electrons transferred, (F) is Faraday's constant, (A) is the electrode active surface area, (k_0) is the heterogeneous electron transfer rate, and (C) is the concentration of the redox species.

Double layer capacitance is when an electrode and a liquid solution are touching each other, causing the charges to line up and allowing electricityto be stored there. The double layer is created when the electrode's surface is charged through the application of electricity. This causes oppositely charged molecules to be attracted to the surface (since opposites attract). This first layer is well attached to the electrode surface, causing it to be semi-permanent. The second layer (with opposite charge) is held by this firstlayer, making it less attached to the electrode than the first layer . These two layers are separated by a single atomic layer of uncharged molecules in the solution. These alternating layers of charges have the ability to store electrical energy, in a way that depends on the amount of electricity initially applied to the electrode. It is denoted by Cdl

Warburg impedance, denoted as ZW, is a complex element in electrochemical impedance spectroscopy (EIS) that represents the mass transfer difficulties of redox species to the electrode surface, assuming a semi-infinite linear diffusion12. It is characterized by a straight line with a slope on a Nyquist plot, indicating a 45° phase angle over the low- frequency range. This impedance element is frequency-dependent and behaves like an RW - CW circuit in series, where both RW (Warburg resistance) and CW (Warburg capacitance) vary with frequency

Constant Phase Element: The origin of CPE has been widely attributed to the surface roughness of solid electrodes, which in turn causes an uneven distribution of various properties, such as the solution resistances, interfacial capacitances, of current densities etc. across the electrode surface.44 However, related models have not been sufficiently supported by experimental data. Most of these models lead to a CPE behavior, however at a rather limited frequency range. Indeed, studies between electrodes with different roughness have shown that the increase of the electrode roughness leads to a CPE behavior closer to the ideal case. The behavior of CPE has also been attempted to be explained by fractal theory.49 Related models succeed to explain the behavior of CPE at blocking electrodes (models generate a linear spectrum tilted with respect to the imaginary impedance axis); however, in the presence of a redox probe, they predict asymmetric (skewed) semicircles instead of depressed semi circles obtainedexperimentally. Other theories, supported by experimental data, indicate that the origin of CPE is related to the mixed (fast) diffusion- (slow) kinetic- controlled adsorption of ions or other impurities of the electrolyte to the electrode surface. This explanation is also in line with experimental data showing that electrodes with increasing roughness exhibit lower deviation (the exponent n is closer to unit) in the sense that at a higher surface the coverage due to the adsorbed ions or impurities is smaller. Theta = 90* (1- n) can be shown in fig 4.12 can also be represented by n=1/(D-1) D is Fractal Dimension For Plane 2D it IS 2 which is for flat electrode with electro with cracks and holes D=3 so becomes n=0.5 .

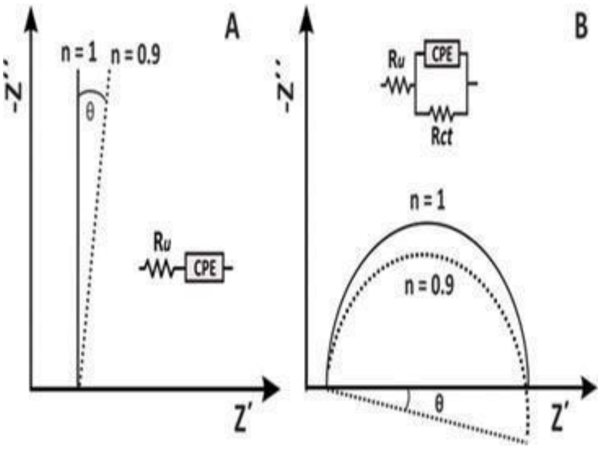


Figure 4.12 :CPE behavior change of angle from idle case

EIS of PG & ACPG

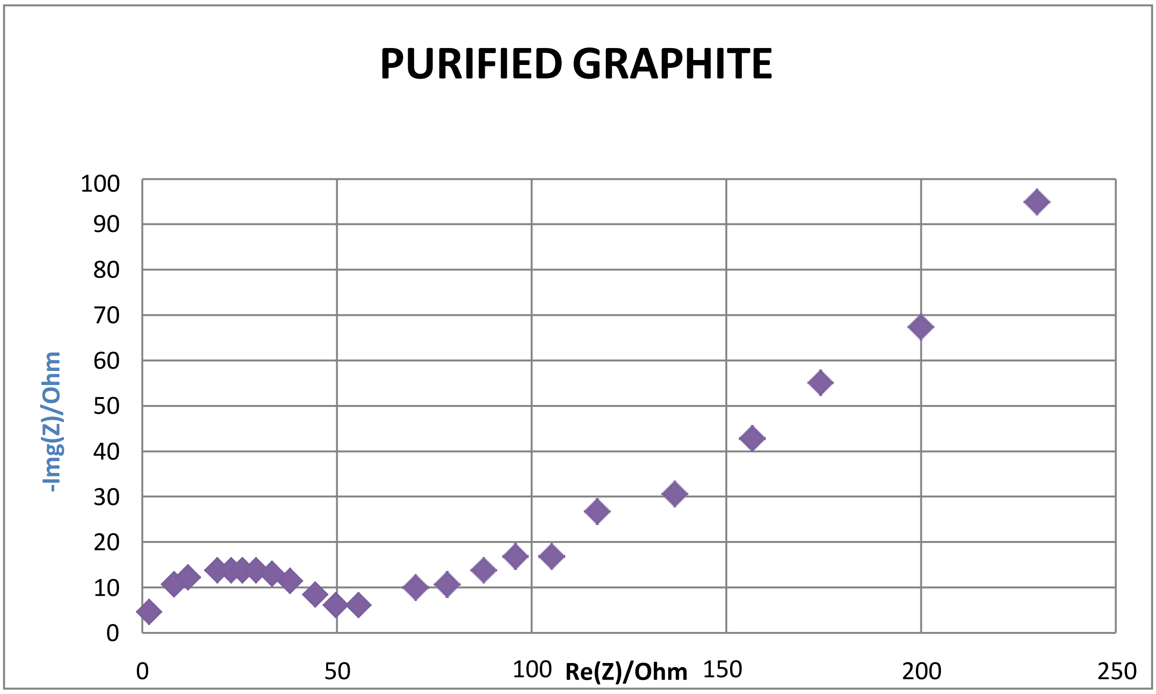


Figure 4.13 : EIS Of Purified Graphite

The **Rct** of PG is approximately **55** ohm as from fig 4.13 which is more than **35** ohm in commercial graphite which is available for different database. The **Electrolytic resistance** is approximately **1** ohm from fig 4.13.

High charge transfer resistance in recycled graphite can be attributed to severalfactors:

Surface Morphology: Purified graphite often has a coarse and uneven surface, which can hinder the efficient transfer of electrons and lithium ions during the charge and discharge process. smoother surface morphology with fewer holes and cracks leads to a lower charge transfer resistance, facilitating faster electron and lithium-ion transport during battery operation. Cracks and holes can disrupt the conductive network within the electrode, making it more difficult for electrons and lithium ions to travel through the material.

Surface Defects: The presence of surface defects and structural damagein purified graphite graphite can increase the resistance to charge transfer, as these defects can act as barriers to ion movement. These imperfections can hinder the proper infiltration of the electrolyte, which is necessary for efficient ion transport during the charge and discharge processes.

SEI Film Formation: The formation of a solid electrolyte interphase (SEI) film on the surface of recycled graphite can also contribute to higher charge transfer resistance. This film can impede the movementof lithium ions, leading to increased resistance.

Impurities: Residual impurities from the recycling process, such as metal particles or organic compounds, can interfere with the electrical conductivity of the graphite, resulting in higher resistance.

These factors can collectively contribute to the higher charge transfer resistance observed in purified graphite compared to pristine graphite materials. Improving the surface morphology, reducing defects, and ensuring the purity of recycled graphite are essential for enhancing its electrochemical performance.

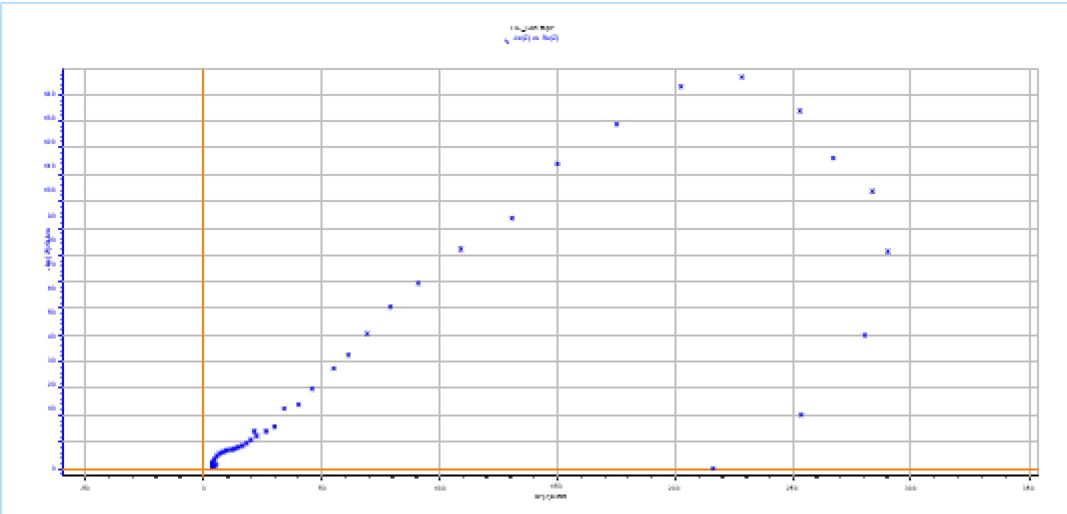


Figure 4.14 : EIS Of Asphalt Coated Purified Graphite

From the fig 4.14 the charge transfer resistance of ACPG is **31.75 ohm** which is less than the that of the PG which is **55 ohm** from fig 4.13 and is approximately equal to purified graphite because of following reason:

Carbon-Coated Network: The asphalt coating undergoes carbonization, creating a conductive carbon layer that encapsulates the graphite particles because of Sp2 and Sp3 hybridize carbon atom .

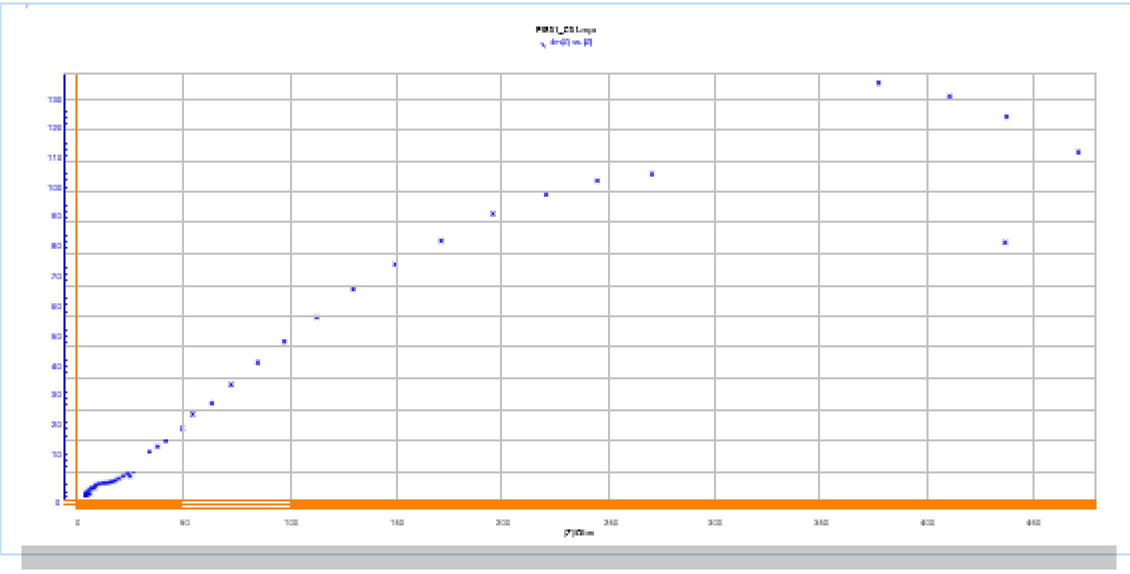
Improved Electrical Conductivity: This carbon layer facilitates better electronic conduction paths, which are essential for the rapid transfer of electrons during the charge and discharge processes.

Enhanced Lithium-Ion Transport: The carbon coating also helps in maintaining a stable structure during cycling, which can reduce the impedance associated with lithium-ion diffusion.

This network provides a continuous path for electrons, reducing the resistance to electron flow and thus lowering the charge transfer resistance. As it enhances electrochemical reaction. We can also observe CPE in the circuit due to depressed circle which s due to small and not flat electrode.

Analysis of finite diffusion of eis model of both:

In this case the Electrolyte is 1 M Solution of Sodium Sulphate The reference Electron is Platinum Electrode.The working Electrode is the graphite coated copper plate. Counter Electrode is Silver Nitrite.Here we can see the finite diffusion and finite Warburg impedanceThe Finite Warburg Impedance is observed when diffusion occurs over a finitedistance It's characterized by a diffusion layer of known thickness .The impedance of FWI tends to the value of (Z_0) at low frequency, which is the resistance at the end of the transmission line representing the finite diffusion path1.The FWI is associated with a trans missive boundary (Warburg Short) or a reflective boundary (Warburg Open), each having distinct equations to describe their behavior. And because of no charge transfer we see no semi-circle and no charge transfer resistance and double layer capacitance from the fig 4.14 and fig 4.15.EIS of ACPG have less charge transfer resistance.



4.3.2 RATE CAPABILITY

Rate capability in the context of batteries refers to the ability of a battery to charge and discharge at different rates. It is an important performance metric that indicateshow quickly a battery can be charged or how much power it can deliver at a given time. Rate capability is the measure of a battery's ability to operate at various current levels relative to its maximum capacity. Here we done rate capability at different current density of 0.1 C to 2c with 5 cycle each.

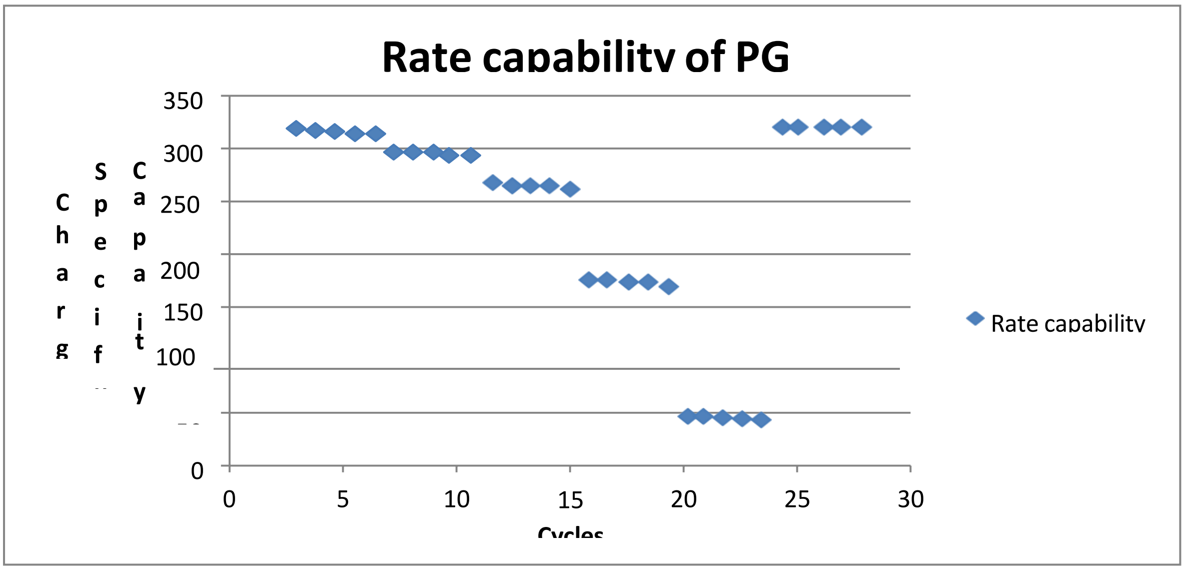


Figure 4.16: Rate Capability of Purified graphite

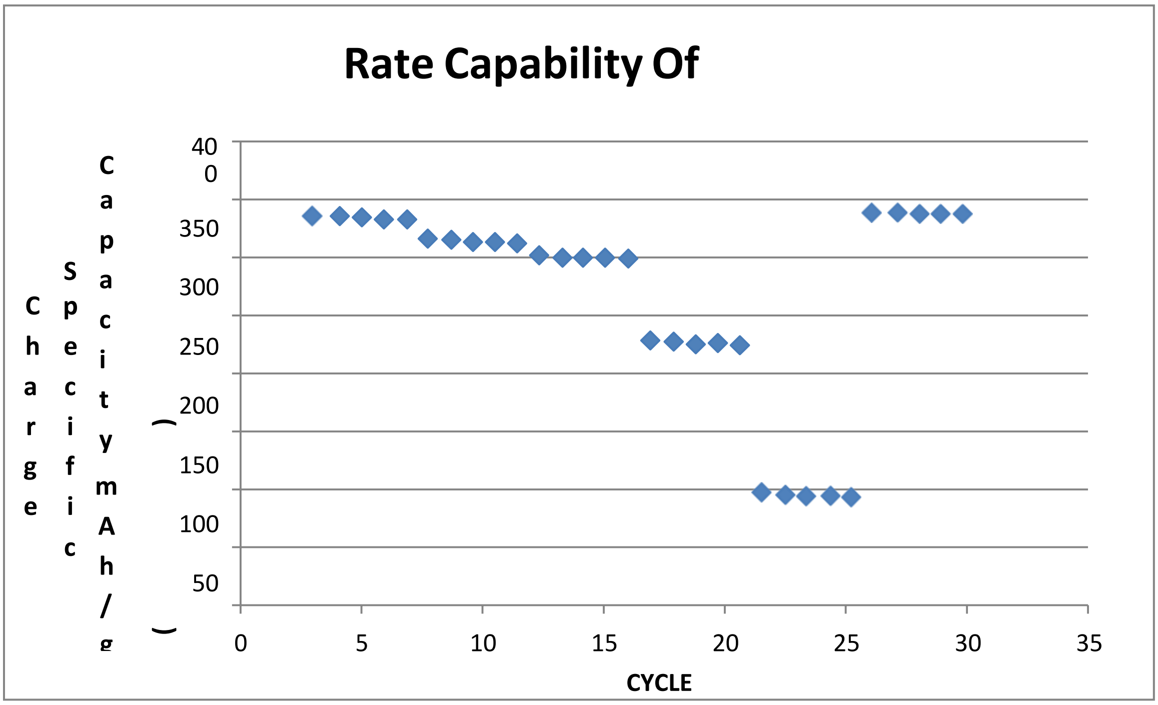


Figure 4.17: Rate Capability Of Asphalt Coated Graphite

From the fig 4.16 and fig 4.17 the specific charge capacity of ACPG is 335 mAh/g which is more than PG which 318mAh/g. The reason are as follows:

- The asphalt-coated graphite shows a higher capacity compared to pristine graphite (PG) under the same conditions. This is attributed to the amorphous carbon network formed by the asphalt coating, which provides aconductive path for electrons.
- Electron Transfer: The amorphous carbon network allows electrons to transfer more efficiently and find the path of least resistance to the internalgraphite.-
- Lithium-Ion Reduction: The efficient electron transfer facilitates the reduction of more lithium ions (Li+) to form LiC6 within a given time frame, enhancing the rate capability of ACPG compared to PG.

In summary, the improved rate capability of ACPG is due to the amorphous carbon network structure that enhances electron transfer and lithium-ion reduction, leading to better battery performance. This is particularly important for high-demand applications where quick charging and discharging are essential.

Chapter 5

Conclusion

The conclusion of the study on improving the electrochemical performance of spent graphite by asphalt coating is as follows**:**

Optimal Coating: The best electrochemical performance was achieved with a 26% asphalt coating, resulting in an initial capacity of 335 mAh/g at arate of 0.1 C2.

Enhanced Performance: Asphalt coating significantly improved the rate capability and initial coulomb efficiency of the spent graphite.

Surface Improvement: The coating process enhanced the surface morphology of the graphite, making it more conducive to electrolyte infiltration**.**

Industrial Prospects: The asphalt coating method is presented as a facile, effective, and economical approach with potential for industrial application in recycling spent graphite and Then again can be Used for making anode in LIB.

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