DEVELOPMENT AND APPLICATION OF CARBON-BASED NANOMATERIALS TO IMPROVE THE PERFORMANCE OF LEAD ACID ENERGY STORAGE DEVICE

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DECLARATION

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Abstract

Lead-acid batteries with conventional materials are now no longer able to meet the emerging requirements for several applications in telecom, automobile, solar, etc., Due to the increase in the demand for higher performances, batteries keeping with the change in the CO_2 emissions, carbon-based materials, which are of possible consideration, are investigated to meet the requirements. The areas in which the lead acid battery is more affect are is the sulphate growth or the grid growth of the current collectors and sulphation in the negative electrode.

Several types of carbon with low and higher dimensions have been attempted to study the electrical performances in the negative plates of lead-acid batteries (LAB). Attempts were made to improve discharge capacity, charge acceptance & life cycling ability of the LAB. Out of many types (2D) Graphene has been selected to evaluate the performance of the LAB due to its unique characteristics. The Carbon Black was commercially purchased as the negative active material additive for the performance comparison, and graphene has been synthesized in our laboratory.

Production of Graphene in Bulk form through chemical methods is a significant drawback of graphene-related research, which is hindering its commercialization. In this work, various chemical methods for the synthesis of graphene were examined, like the Hummers method, Modified Hummers method, and Microwave-assisted acid method. The results were very accurate by the microwave-assisted acid method. The productivity and purity of the produced graphene using this method are very high. The Morphology, Structure, and Phase characteristics were well studied by using various characterization techniques like XRD, SEM/EDS, Raman, and BET.

Along with Graphene layers, which were synthesized by microwave-assisted method, the commercially purchased carbon black was also used as part of the electrode material

validation for energy applications. The carbon-based nanomaterial is used as an additive for negative electrode material for absorbed Glass Mat (AGM) lead-acid batteries.

For making an electrode for lead acid battery application, electrochemical & electrical studies are essential to rationalize.

In one aspect, to address the premature failure (PMF) due to the grid surface, the graphene material is prepared in the colloidal for and applied to the grids. A 2V cells was assembled to study the coated grid performance and found the positive coated grid has better electrical behavior than the negative coated grids. This higher-rated capacity is prepared with positive coated grids (2V-600Ah). The electrical tests at lower rates 0.1C, 0.5C, and 1C are marginally higher than the uncoated grids. But at higher current discharges for shorter durations like C15 minutes and C5 minutes, the positive coated grids outperformed by 2 to 3 times, respectively.

In another aspect, Graphene was prepared and applied in negative active material of AGM lead acid battery, and studies were carried out. Other individual components of the composite like $BaSO_4$ & Lignin are used to integrate the low dimensional carbon as an additive composite and are dry mixed with the active material (Lead Oxide) and applied to the lead grid used as current collectors.

By the experimental investigation as per Japanese Industrial Standards (JIS) the electrical performances, it is observed that the current discharge capacity increased by nearly 27% with graphene as an additive in NAM.

Whereas in charge acceptance capability enhancement of 14% is observed, and the time taken for discharge capacity of the batteries with Graphene has exceeded the requirement and for a long-time-interval of 23%, respectively.

The cycle life of the graphene batteries increased by 33% compared to that of the control batteries above the 40%SoH condition.

The results demonstrated that the component particles are uniformly distributed towards the nanomaterials; this tells the proper formation of the composite. Electrochemical studies

of graphene nanomaterial electrode reveal that the impedance characteristic is very different from that of traditional one. Therefore, the electrical performances are evidence of these materials having the ability of electrode material properties for energy applications.

Keywords: Carbon; Nanomaterial; Graphene; Lead Acid Battery; Lead Grids; Negative Active Material; Premature Failure (PMF); Progressive Failure (PGF); Sulphation; Stationary Lead Acid Battery; Automotive Lead Acid Battery; Japanese Industrial Standard (JIS); High Current discharges; Energy density (Capacity); Charge Acceptance; Cranking Ability; Charge/Discharge Cycles.

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During the course of the project work and during the preparation of this manuscript, I referred to several valuable books, journals, and technical papers listed in the References. I wish to thank all the respective authors.

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NOMENCLATURE

A - Area

c - capacitance

C15min - Capacity Ampere-Hour Rating at 15 minutes

C5min - Capacity Ampere-Hour Rating at 5 minutes

C1 - Capacity Ampere-Hour Rating at 1hour

C5 - Capacity Ampere-Hour Rating at 5 hours

C8 - Capacity Ampere-Hour Rating at 8 hours

C10 - Capacity Ampere-Hour Rating at 10 hours

CAT - Charge Acceptance Test

CCA - Cold Cranking Ampere

CV - Cyclic Voltammetry

DoD - Depth of Discharge

EV - ElectriC Vehicle

E^o – Standard Cell Potential

GO - Graphene Oxide

H_2O - Water

HEV - Hybrid Electric Vehicle

HLE - High Load Endurance

HRD - High-Rate Discharge

HRPSoC - High-Rate Partial State of Charge

H_2SO_4 - Sulfuric Acid

ICE - Internal Combustion Engine

LAB - Lead Acid Battery

LAESD - Lead-Acid Energy Storage Device

LLE - Light Load Endurance

m = Mass

$NaOH$ - Sodium Hydroxide

PAM - Positive Active Material

NAM - Negative Active Material

PSoC - Partial State of Charge

Pb - Lead

PbO - Lead Monoxide

PbO_2 - Lead Dioxide

$PbSO_4$ - Lead Sulfate

$Pb(OH)_2$ - Lead Hydroxide

Pb_2O_3 - Lead Trioxide

Pb_3O_4 - Red Lead

Q - charge

rGO – Reduced Graphene Oxide

Sb - Antimony

SE - Secondary Electron

SEM - Scanning Electron Microscopy

SLI - Starting Lighting Ignition

SoC - State of Charge

SSA – Specific Surface Area (m^2/gm)

Sn - Tin

XRD - X-ray Powder Diffraction

3BS - Tribasic Lead Sulfate

4BS - Tetrabasic Lead Sulfate

R - Resistance, ohms

T - Temperature, ^0C

v - Scan rate

V - Potential Window

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INTRODUCTION

1.1 General Background

Almost every automobile which runs on IC engines/Electric Vehicles has a Lead-Acid Battery (LAB) as a power source for Starting the engine/motor, Lighting/ Turn on the Electrical equipment's and Drive. In general, a battery is an electrochemical device which store energy in the form of chemical state later converting into electrical form in discharge condition and back to chemical energy at recharge condition. Compared to the available different types of battery technology in society today, Lead-Acid battery is one of the commonly used devices due to its mature technology for reliable energy supply. Usually, Lead-Acid batteries are the most cost-effective and safe in operating technology suitable to various applications like Stationary, traction, Hybrid/Electric vehicles, etc.,

Although the Arsacid empire used electrochemical cells in late 247BC mentioned by A, J. Salkind, the usage of lead/Lead dioxide/Sulfuric Acid was primarily identified with the invention of lead-acid energy storages in 1859 by the renowned French physicist Gaston Plante. However, the foundations for the electrochemical cell discoveries were laid by Luigi Galvani, a medical professional from the University of Bologna, Italy, in the 1780s. Later, Alessandra Volta, in 1796's who had displayed the first primary (Irreversible) cell/battery. To their works and contribution towards electrochemical innovations, the Cell/Battery are termed as "Galvanic / Voltaic Cells." Right from its inception to date, the lead-acid battery is the best-known rechargeable energy storage solution of choice for most automobiles & other industries due to its cost and safety benefits.

Lead-Acid Batteries (LAB) are used in a wide range of applications like a power source in a motor vehicle, UPS systems, Telecommunication, and many more applications with increasing demand a constant and uninterruptible source of energy. Usually, Lead-Acid batteries for automotive applications consist of 6 cells, each cell delivering 2 volts, with 12 Volts when connected in series. The cells consist of lead alloy plates that are positive and negative electrodes. Positive and negative plates stacked alternately negative/positive/negative with suitable quality separators placed between the plates to prevent short circuits as essential components shown in the figure below fig.1. The more plates in a cell, the higher the current capacity. The design of Lead-Acid Batteries is simple; the electrodes in each cell are arranged alternatively with one positive and one negative electrode. Each cell group of 6cells electrodes are then connected in a series like Positive to Negative / Negative to positive manner. Electrolyte solution, i.e., dilute sulfuric acid, is added, then chemical action starts. A reaction between the electrodes and the electrolyte creates an electrical charge. The transfer of ions (H^+ & $SO^-{}_4$) occurs during the battery's charge/discharge. The electrolyte's specific gravity tends to change during the charge/discharge period. In the Discharge state, the changes in the electrolyte gravity happen when free Sulfate ($SO^-{}_4$) ions are drawn into the pores of the battery electrodes from the sulfuric acid electrolyte; this leads to a reduction of the specific gravity of the electrolyte with an increase in the water concentration. In the charge condition, the reversible reaction occurs, where the sulfate ions are passed out from the battery electrodes back into the electrolyte and increase the gravity of the electrolyte. During the above-said discharge process, the sulfuric acid is used up, and Lead Sulfate is formed on the battery electrodes. This is the natural process within the battery during discharge. Battery recharging is necessary to avoid hard sulfation or conversion of lead sulfate crystals into the sulfuric acid electrolyte. If irregular recharges are done, the hard lead sulfate crystals will continue to develop and become difficult to break down at recharging conditions. This will lead to a progressive failure, which then the battery becomes an unusable mode. Many other dendrites (detrimental) actions occur on the surface of the battery electrode while in a discharged condition. The corrosion effect on the lead grids and the connectors increases with the reduction of the electrolyte specific gravity. State of charge during long periods of storage time must be checked and maintained as per the manufacturer's instructions. Several other conditions that can lead to battery failure are inadequate charging or having the battery in idle/inoperative condition for prolonged duration in the vehicle. Overcharging and internal battery temperature should be avoided to ensure optimum life. The addition of distilled water externally is required to have a long life of the battery. At longer charging, the failure of effective Hydrogen and oxygen recombination leads to Water loss, which is typical in lead-acid batteries. This process is also termed as electrolysis as the evaporation of Hydrogen takes place. Lower electrolyte levels or unfilled space which exposes the lead electrode in operation will result in quick failure of the battery immediate with capacity loss and other to follow. LAB requires to maintain the electrolyte levels over the top of the electrodes /above the minimum marking lines mentioned on the outer plastic case of the battery. VRLA/AGM (Valve-Regulated Lead-Acid / Absorbed Glass Mat) battery has a fixed quantity of electrolyte added at the manufacturer. Once the battery is permanently sealed and charged, it must be never opened until its end life, the opening of the LAB is restricted due to safety and environmental conditions. Currently, AGM technology holds the market demand. Based on AGM (Absorbed Glass Mat) technology, the batteries offer good electrical performance characteristics when compared to flooded technology. The AGM batteries are used in a wide range of applications such as Power backup, Electric/Hybrid Vehicles, Traction, Emergency Lighting, et cetera.

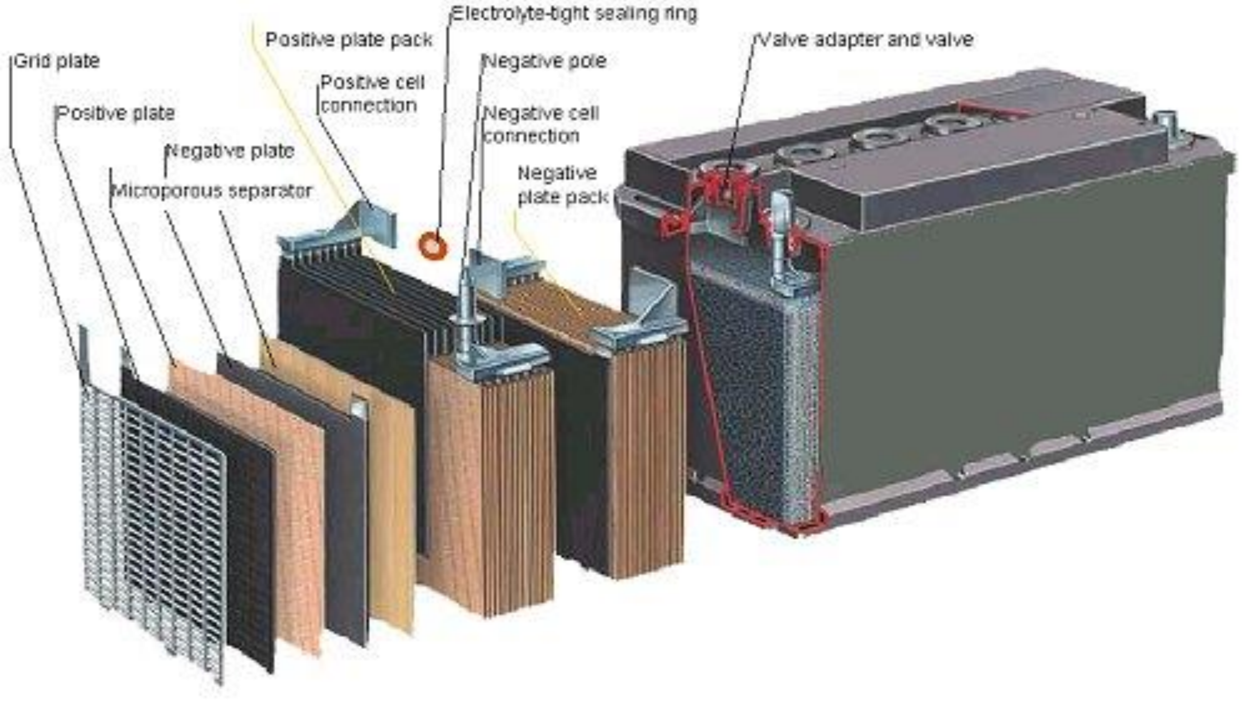


Fig. 1.1 Components of Lead Acid Battery.

1.1.1 Lead-Acid energy storage Construction

Six Lead-acid (Galvanic) Cells are interconnected in a series fashion to obtain a typical 12-volt lead-acid battery. Where these cells are enclosed in a plastic container with six compartments, each cell comprises of two different types of electrodes one being the anode (negative) lead (Pb) electrode and the other being the cathode (positive) lead dioxide (PbO_2) electrode. These two electrodes are separated by an insulating material, either AGM or Polyethylene (PE) Separator.

a) Electrodes

A typical lead-acid battery electrode contains Lead Oxide (PbO) as active material, used in the reduction-Oxidation reaction, and a current collector grid made of Lead (Pb) Alloy, as shown in fig. 1.2. As the metallic lead (Pb) is malleable, alloying additives like Tin (Sn), calcium (Ca), antimony (Sb), et cetera, are used to create lead alloys to enhance the electrochemical properties of the battery. The combination of the Lead alloy grid and the lead oxide Active Material (AM) form a plate/electrode. After the formation process, the lead oxide in the positive/cathode (+Ve) electrode becomes lead dioxide and Lead/spongy lead at the negative/anode (-Ve) electrode.

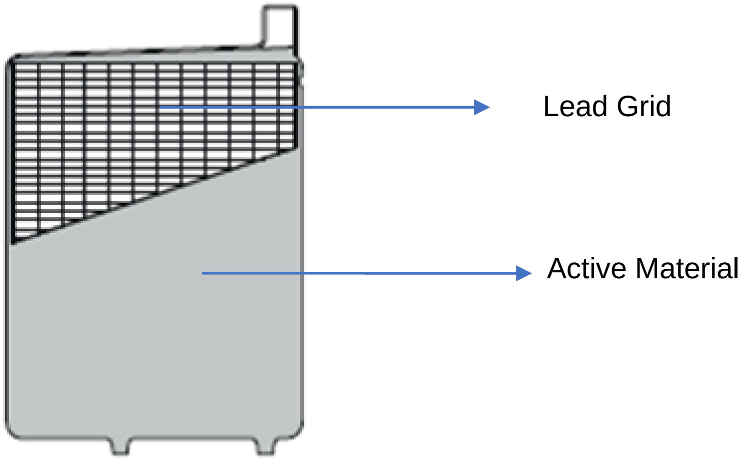


Fig. 1.2 Battery Current Collector.

b) Electrolyte

As mentioned earlier, the electrolyte is a diluted Sulfuric Acid (H_2SO_4) which is used in the lead-acid battery. The Concentrations of acid are varied with the designs, but generally 30 to 40% of weight is used in the battery. Generally, electrolyte exists as positively charged hydrogen ions (H^+) and negatively charged sulfate ions ($SO^-{}_4$), which acts as a crucial ingredient in redox reactions. In other designs, treated silica (SiO_2) along with other additives are added to the electrolyte to create a gel from and termed as Gel batteries. In AGM batteries the electrolyte can be trapped and can be used as required, with this design, there are several advantages, like the electrode cells can be mounted in any orientation without any maintenance. In other designs, distilled water needs to be added for prolonged life.

c) Separator

The primary role is to insulate the positive and negative electrodes. The separator is of a porous membrane that prevents the dendrites by reducing the shedding of the active material, causing a short circuit. Majorly, there are two types of separators in lead-acid designs: microporous membrane made up of polyethylene and other absorbed glass mats (AGM) by silica. The microporous membrane present allows the free flowing of electrolytes in flooded form. However, the AGM consists of glass fiber and is soaked in the electrolyte; the fiber absorbs the acid and tends to sink into the solution. Therefore, the advantage of AGM when submerged in the electrolyte solution is that it provides the stability of avoiding electrolyte spills and stratification.

As discussed earlier, the Lead-Acid Battery consists of the following components: we can see in the below Fig. 1.3

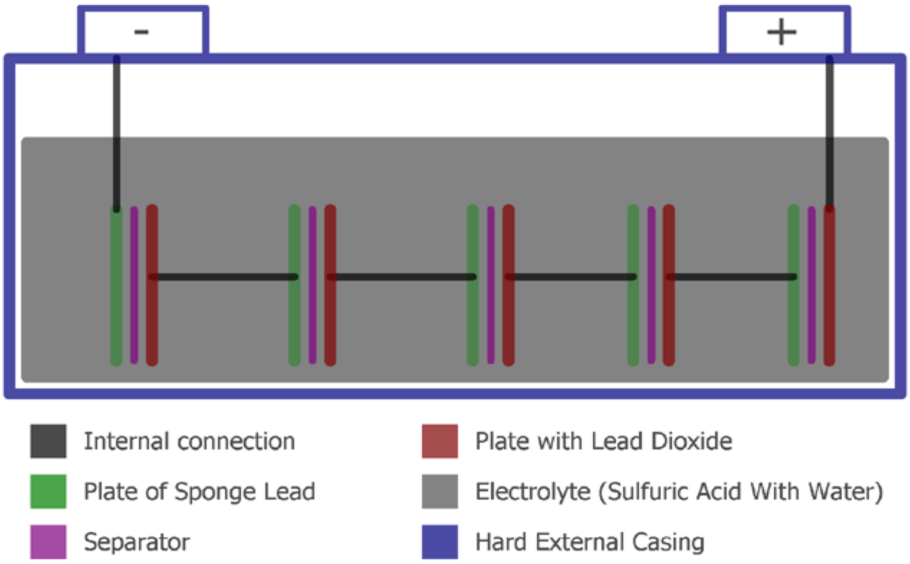


Figure 1.3 Lead Acid Battery Construction
(Image source: www.circuitdigest.com)

The components of a Lead Acid Battery are Positive and Negative Electrode/ Plates, Separator, and Electrolyte enclosed in a rigid plastic container. A compartment in the plastic container holds a 2V design with the above-said components. Due to this, a series of 2V is connected to make a 12V lead-acid battery (6 x 2V/cell = 12V).

Although lithium-ion batteries seem to grab most of the headlines these days, lead-acid has long been the go-to chemistry for renewable energy storage. Despite their size and weight, lead-acid batteries can deliver enormous amounts of power more cost-effectively than any other energy storage.

Tomorrow's electric grid may require higher energy storage to incorporate more copious quantities of intermittent renewable energy resources. In recent times, LAB has been used as backup power in off-grid applications. Certain limitations in the cycling for these applications need to be addressed as the battery cycles from a charged to the discharged state and then back to a fully charged state, the lead and lead dioxide react with the sulfuric acid electrolyte in the battery, which produces the lead sulfates in the electrodes, known an as sulfation. Over a period, these crystal sulfates accumulate on the negative electrodes and hinder the reversible reactions. Therefore, the battery is limited to perform at different cycle rates.

1.1.2 Electrochemical Reactions of LAB at different stages:

a) Initial Reactions: At electrode preparation where the active material basically lead oxide (PbO) is mixed with sulfuric acid along with binder (Polyester). And carried out with curing process. The application of the batteries requires the either 3BS/4BS crystals in the electrode for effective formation and higher active material utilization. 3BS is required for automotive application and 4BS for stationary application.

$PbO\ (AM) + H_2SO_4 = PbSO_4 + H_2O$ (1)

Curing Environment @ $<70^{o}C$: $PbSO_4 + 3PbO = 3PbO \cdot PbSO_4$ (3BS) (2)

Curing Environment @ $>70^{o}C$: $PbSO_4 + 4PbO = 4PbO \cdot PbSO_4$ (4BS) (3)

b) Formation of the cells: At Finishing Stage the formed lead sulphates (PbSO4) is further converted to lead dioxide (PbO2) in the positive electrode and lead (Pb) in the negative electrode.

+Ve Electrode: $PbSO_4 + 2H_2O = PbO_2 + H_2SO_4 + 2e^- + 2H^+$ (4)

-Ve Electrode: $PbSO_4 + 2e^- + 2H^+ = Pb + H_2SO_4$ (5)

c) Discharging/Charging: At indiviaul electrodes the electrochemical reations takes place at operation as shown in the Fig 1.4 giving out a 2.04 potential difference across the electrodes.

-Ve Half Cycle: $Pb + H_2SO_4 \leftrightarrow PbSO_4 + 2H^+ + 2e^-$ (E^0 = ~0.356 eV) (6)

+Ve Half Cycle: $PbO_2 + H_2SO_4 + 2H^+ + 2e^- \leftrightarrow PbSO_4 + 2H_2O$ (E^0 = ~1.685 eV) (7)

Both the half cycles contribute to the total voltage of Eq. (1) + (2): 2.04eV

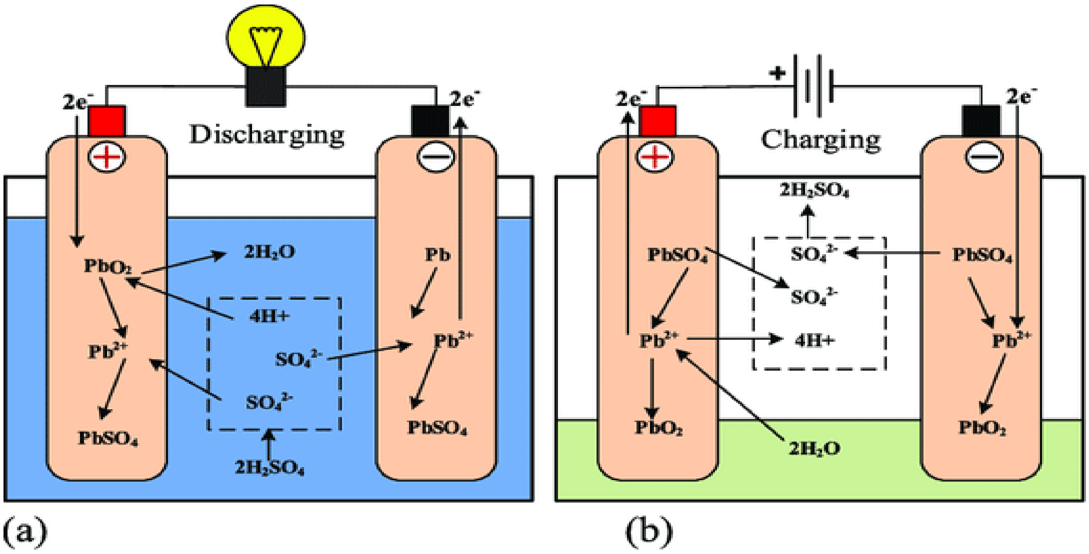


Fig. 1.4 Operation of Lead-acid battery (a) Discharging (b) Charging.

1.1.3 Current challenges for Lead Acid Battery

Apart from manufacturing flaws, emerging needs like Hybrid/Electric Vehicle demands higher current charge and discharges, leading to a development of advanced lead-acid battery performance to suit the requirements. Due to this, the battery is stressed out in impacting the performance. The two major areas that hinder the emerging requirements are:

1. **Premature failure of the battery:** Where the development of high resistive film between the lead grid and the active material of the positive (Cathode) grid hindering the performance of the battery, specially at high-current discharges. This further leads to grid corrosion and permanently damage the battery performance.
2. **Progressive Failure of the battery:** This is where the rapid sulfation growth happens in the negative electrode, leading to irreversible hard sulfates formation withing the active material and on the surface of the electrode, at rapid continuous charge/discharge condition.

Generally, flooded/AGM batteries are used for Start Light Ignition (SLI) as one of the applications in the automotive industry. As the demand for higher performances evolves, the possibilities of failure modes also increase. As mentioned above, the main area of failures is the progressive sulfation and the development high resistive film interface with the lead grid (Premature failure). Targeting resistive film and the sulfation of the electrode to overcome the barriers is by the addition of carbon in nano form.

Recently several industries are studying the use of low dimensional carbons, especially carbon nanomaterials, as additives in lead-acid batteries and advantages on charging and discharging capacities. The studies include the effect of carbon particle sizes in the porous active material on cycling capabilities at different state of charge (SoC) conditions.

1.1.4 Nanotechnology – A possible solution for Energy Storages

Nanotechnology is the study of materials whose dimensions (at least one) range from 1nm to 100nm. This study of microscopic dimensions and tolerances (less than 100nm) can be applied in all other science fields such as biology, chemistry, medicine, material science, and engineering. Nanomaterials are highly reactive due to the high surface-to-volume ratio. They behave completely differently from their bulk counterparts. They show improved properties (electrical, mechanical, thermal, etc.). Using nanocomposites (at least one material is in the nano range) can enhance properties and reduce the size (portability). Carbon is a vital material system with different allotropes. Graphite and diamond are the commonly known allotropes. Recently other allotropes of low dimension carbon (like Fullerene, a nano form of carbon) are discovered like 0D, 1D, 2D & 3D, as shown in Fig. 1.2. These carbon nanomaterials with improved properties are promising materials for energy storage applications. New-age carbon nanomaterials include graphene, carbon nanotubes, fullerenes, etc., among which graphene and its related forms have gained considerable popularity owing to their unique properties.

a) Carbon Materials as Lead-Acid additive:

As said, there is an increasing demand for high-performance capability with respect to the automobile industry. Now the lead-acid battery industries are in search of exploring carbon nanomaterials for enhancing the performances of the batteries. Carbon materials are used to lay a conductive network in Lead-acid batteries to suppress sulfation occurring on the surface of the negative electrodes at high discharge capacity. Due to sulfation, the life of the batteries is limited to short durations, impacting the lead-acid battery industries. The inhibition process by the carbon relies on the size of the sulfates, where the large sulfates formed during high discharges are not reduced back to lead metallic constituents. There have been some attempts to reduce and restrict the size of the sulfate crystals by using nanocarbons. This has led to maintaining the $PbSO_4$ crystal size as minimum as possible by using of low dimension carbon materials. Various Carbon allotropes have been explored by different research groups for increasing the specific energy and the performance of charge acceptance & high discharge studies as per Japanese international Standards (JIS). The low cycle life, water loss & self-discharges of the lead-acid batteries is due to the lack of purity in carbons resulting low recombination rate of hydrogen onto the negative electrodes. The high structured carbon nanomaterial as additives would help the transportation of ions in the electrode and enhance the active material utilization (specific energy) for higher cycles.

Researchers find carbon to be incorporated into the lead-acid design in various configurations. One technique is to blend the carbon additives into the lead oxide paste, making the negative electrodes. Alternatively, the regular lead grids used for pasting can be replaced with colloidal carbon on the surface of the lead grids before being taken to the pasting. This hybrid design dramatically improves cycle life over traditional lead-acid batteries.

b) Graphene and its importance

Out of all nanocarbons, Graphene is the most suitable material because it is a 2-Dimensional material which can accommodate maximum interaction with the active material in electrode preparation of LAB. And holds the unique characteristics due to its preparation in cost effective manner. Graphene is a two-dimensional layered material where carbon atoms are bonded with sp^2 configuration in a hexagonal closed packed system (HCP), which belongs to graphite family. The figure 1.5 shows that the graphite allotropes of carbon atoms packed densely in a honeycomb lattice. Since its discovery, which lead to Nobel prize in 2004, graphene has attracted much attention from scientists due to its unique properties. Graphene is the most durable material ever produced, with superior thermal and electrical properties. It indicates that it is suitable in potential applications like electronic devices, aerospace applications, automobiles, etc.

Single layer Graphene material has a large theoretical surface area of ~2630 m^2g^{-1}, exceeding graphite surface area (<10 m^2g^{-1}). This higher surface area compared to other materials makes it possible to store more charges which can improve the performance of the energy storages.

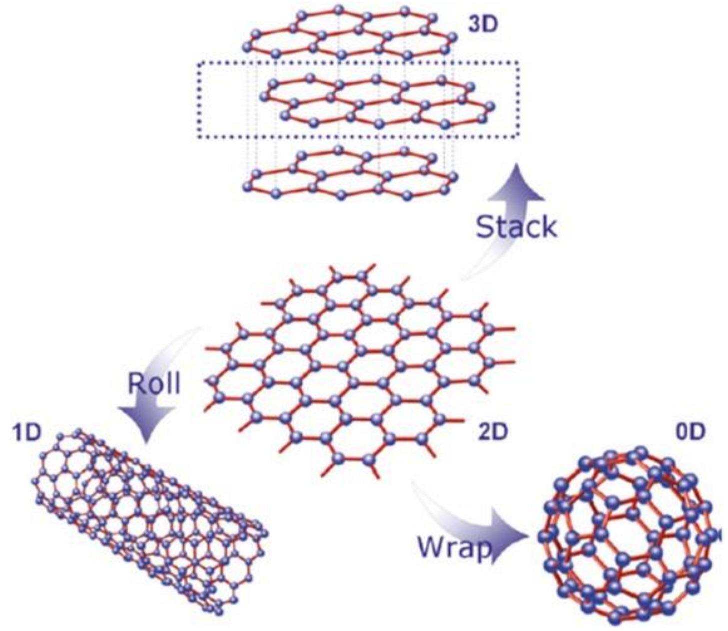


Fig. 1.5 Carbon Allotropes:- (0D) Fullerene (1D) Nanotube (2D) Graphene (3D) Few layer graphene (FLG) or Graphite [Image reproduced from Wan et al. (2012) with permission of American Chemical Society]

The below properties which the graphene material is set apart from other materials and makes it unique are:

- Theoretical specific surface area (2360 m^2/g)
- Electron mobility (200,000 $cm^2v^{-1}s^{-1}$)
- Mechanical Strength: The Young's modulus (~1.0 TPa)
- Thermal conductivity (3000 - 5000$Wm^{-1}K^{-1}$)
- Optical transmittance (~97.7%)

Synthesizing 2D carbon material (Graphene) has many routes, which are listed below, and several other facile routes are also emerging.

- Mechanical – Peel-off method
- Atomic epitaxial growth on metal substrates
- Pyrolysis of sodium ethoxide
- Unzipping of carbon nanotubes
- Graphite delamination process

- Chemical Vapor Deposition (CVD), et cetera.

Due to its unique property's graphene is studied in several applications other than energy storage are the few identified areas below:

- Gas detection
- Graphene as transistors
- Touch Screen - Transparent Conducting
- Heat transfer systems
- PV solar cells.

1.2 Objective of the study

Our objective is to address the limitation of traditional lead-acid energy storage and provide a solution by rational structure design according to the below principles and criteria. This aims to develop high-performance lead acid devices for emerging applications for Hybrid/Electric automotive and On/Off-grid storages. The goal is to fundamentally understand the operational mechanism and improve the performances like Specific capacity (Ah/g), charge acceptance, High current discharge & life cycle of the lead-acid batteries. Generally, this proposed work is dedicated to the following aspects:

1) Understand and explore the mechanism/behavior of the materials of lead-acid energy storage.

2) Fundamentally and technically find the bottlenecks of current carbon materials for Lead-acid energy storage.

3) Develop and implement the novel synthetic method to obtain a new class of carbon materials aiming at its current limitations.

4) Fabrication and integration of low dimensional carbon materials into the

battery component and examine their electrical performances.

1.3 Scope of the Present Work

The scope is to improve the high current discharges and charges of the battery. These benefits are achieved by incorporating carbon nanomaterials on the lead grid and in the electrode's active material. This eliminates/reduces the development of the resistive layer and the sulfation in the electrode. This technique could increase the conversion efficiency of the battery in automobile vehicles by significantly increasing the performance of the batteries which need to provide adequate power.

Moreover, it is to increase the cycle life of a battery by using nanomaterials for making the electrolyte availability in the battery from forming the sulfation on the solid electrodes. This also prevents the low-level discharge in a conventional battery, which dramatically increases the battery's shelf life.

Lead Acid batteries with electrodes made from nanostructured carbon significantly improve the cranking ability even at low temperatures.

Batteries using graphene sheets to store electrical charges improve lead-acid batteries' capacity and battery lifetime.

1.4 Organization of the Thesis

Chapter 2 provides a review of the previously published research on Graphene – A carbon-based nanomaterial Both synthesis and application investigations for lead-acid energy storage systems are presented.

Chapter 3 discusses the identification of gaps in the available works of literature and summarizes the scope of the present work.

Chapter 4 describes the methods and the preparation of carbon-based nanomaterials.

Chapter 5 is devoted to summarizing the characterization methods of the prepared material and analyzing the process parameters.

Chapter 6 describes the present investigation, in which an attempt is made to prepare the desired electrode and analyze the electrode behavior before making it into a battery, maintaining the quality protocols as per the industrial standards.

Chapter 7 presented the results and discussed which describes the improvement in the electrical performance of the lead-acid batteries due to the application of carbon-based nanomaterial.

Chapter 8 presents the summary of the research and the major conclusions drawn from these investigations. Further research needs are also identified and presented.

CHAPTER – 2
Literature Review

In this chapter, we will be discussing the works carried out by various research groups in developing advanced lead-acid batteries with carbon materials and the synthesis of 2D carbon nanomaterial with several approaches are discussed. The first part of the chapter discusses about the exploration of graphene synthesis and followed with the key findings of carbon usage in lead acid battery. The summary and the identified gaps were collated and presented.

2.1 Forms of Carbon

As per Sandia National Laboratories, USA report (SAND2011-3459, 2011), the carbon is classified in to two categories as Amorphous and crystalline carbon as shown in Fig. 2.1.

1. Amorphous Carbon (Carbon Black, acetylene black, furnace/Channel/Thermal black & lamp black)
2. Graphitic Carbon (Graphite, Expanded/Exfoliated Graphite, Graphene, Fullerene & Nanotubes)

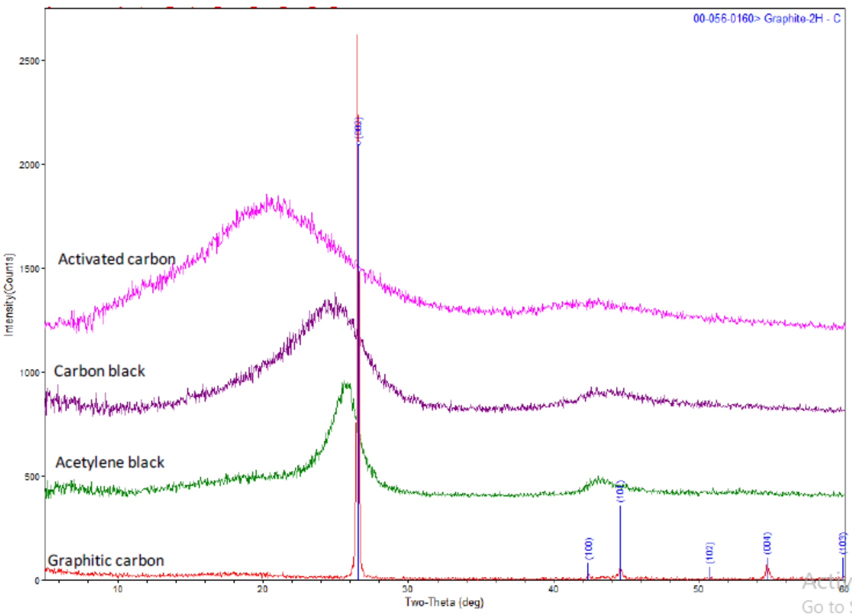


Fig 2.5 (a)X-Ray spectra of Crystalline to amorphous carbon grades – Sandia National Laboratories, USA (2011).

However, the advantages of crystalline carbon are more when compared to amorphous carbons. Due to their structural stability these materials gained attention over the years by several research groups. While the amorphous carbons are heavily produced by oil industries and the crystalline materials like graphite are naturally found and most crystalline carbons are synthetically grown/made. Out of all crystalline carbons graphene has been predominantly investigated due to its unique properties as discussed in earlier chapter. Now, let us investigate the synthesis procedures and the challenges faced by several scientists in making graphene material from graphite.

2.2 Synthesis of Carbon Nanomaterials - For Energy storages

Stankovich et al (2007) had synthesized graphene by reducing the graphite oxide chemically, following colloidal suspension method. The prepared material was characterized by SEM, XRD, Raman, EDAX, Conductivity etc., and confirmed. Further studied by incorporating as conductive filler in the composites for energy storage device.

Kaniyoor et al (2010) had used hydrogen atmosphere to synthesize graphene by exfoliating graphite at low temperatures (<100°C). Later characterized using XRD, SEM, Ram, XPS and N_2 adsorption techniques for physical and chemical properties.

Marcano et al (2010) extracted graphene by oxidizing the graphite flakes with $KMnO_4$ and other acids like H_2SO_4 and H_3PO_4. He also compared with other routes and disclosed that his method leveraged in less defects with high productivity (50% Yield).

Hernandez et al (2009) adopted liquid phase exfoliation by inducing mechanical forces of graphite solution. Graphite is mixed with a surfactant and stirred in water overnight. This solution is later sonicated, centrifuged, filtered and dried to obtain graphene material. Various characterization techniques like microscopic and spectroscopies were followed the formation of graphene material.

Chen et al (2009) has also adopted H_2O_2 as strong oxidizer along with $KMnO_4$ and H_2SO_4 acid allowing the reactions to take place under 20°C. Later stirred at 35°C and washed with HCL solution before drying. The obtained dried powder is then characterized and found to be acceptable, but with more time duration of >2days.

Chung et al (1987) revealed different ways of exfoliating graphite to obtain graphene nanostructures. Three major ways are highlighted by the scientist 1. By using oxidizers and acids creating a exothermic reaction. 2. Subjecting the acid treated graphite to external heating. 3. Allowing the acid treated graphite to mechanical forces like sonication.

G. Venkata Ramana et al (2011) has successfully prepared graphene/PANI composite with high thermal stability and good electrical conductivity for energy application, which found to be reliable.

Zhihong Luo et al (2013) had prepared Graphene/PANI composite for supercapacitor application. The graphene is prepared by reflux method in combination with aniline oxidized by ammonium persulfate (APS). The composite have better capacitance than individual, enabling as supercapacitor electrode.

Srinivasulu Reddy K et al (2015) reported the usage of graphene as metal matrix composites enhances the mechanical and thermal behavior of the composite. A powder metallurgy process has been adapted to make graphene /aluminum metal matrix nano composites (AMMnCs) with enhanced properties.

2.3 Application of Carbon in Lead Acid Battery for progressive failure

Although the foundations laid for the primary batteries (Non-Rechargeable) by Luigi Galvani in 1780's the wide spread of the secondary batteries (Rechargeable) was not seen until Raymond Gaston Plante inventing the lead acid cell in 1859 later named as Plante battery on his memory. Later, several inventions & developments has been made in terms of operations/usage.

The plante's battery consisted of nine cells in parallel and was constructed by winding to led strips with a rubber strip and a heavy lenin or felt material is placed between them s shown in Fig. 2.2. This arrangement was housed inside a cylindrical jar after filling the cells with dilute sulphuric acid the plates were found by using bunsen battery this is akin to plante formation.

The popularity off plant battery increased with the development of electrochemical dynamic by W. V. Siemens et. al in 1866 and with the invention of Magneto electric generator by Societe Gramme et. al around 1873 as cheap reliable and practical sources of direct current for battery charging.

Twenty years after plante discovery of lead acid system Gladstone and Tribe et. al explained in 1881 and 1882 the reactions occurring in the system on the basis of "double sulphate theory" meaning that both lead dioxide and lead were converted into lead sulphates during discharge also this theory met with violent opposition, and it was confirmed by several others.

Around 1919 G Shimadzu et. al in Japan device the forerunner for the present-day ball mills for making lead oxide powder as active material. From 1920 onwards newer applications like emergency power supply air conditioning of rail cars and a host of other services on ships aircraft buses and trucks began to play important role in enhancing the market share of lead acid batteries.

Initial days wood was used as separators. Usage of Expanders began from 1920 and new types of separators were developed to replace the wood separators. When rubber separators were substituted for wood separators the performance of the batteries was not satisfactory and this failure was traced to the lack of wood ingredients in the electrolyte. Soon, finely grounded wood was included in the negative paste composition to obtain superior low-rate high discharge performance. This experiment has let for increased experimentation on the effectiveness of adding additives, which led to the present-day use of carbon, barium sulphate and lignin derivatives.

Breakthrough in the development of commercially viable sealed lead acid battery came after the invention of sealed nickel cadmium cells by Lange et. al. He was the first to outline the principle of oxygen cycle happing by the electrodes in his US patent 1938 then later in 1950s and early 1960s the strong foundations came necessary for the commercial development of sealed batteries. Simultaneously two technologies on one based on gel electrolyte and other absorbed glass mat was developed. The process of fine refinements in the technology is continuing one till date making improvements in several fields of battery evolution as well as in application areas.

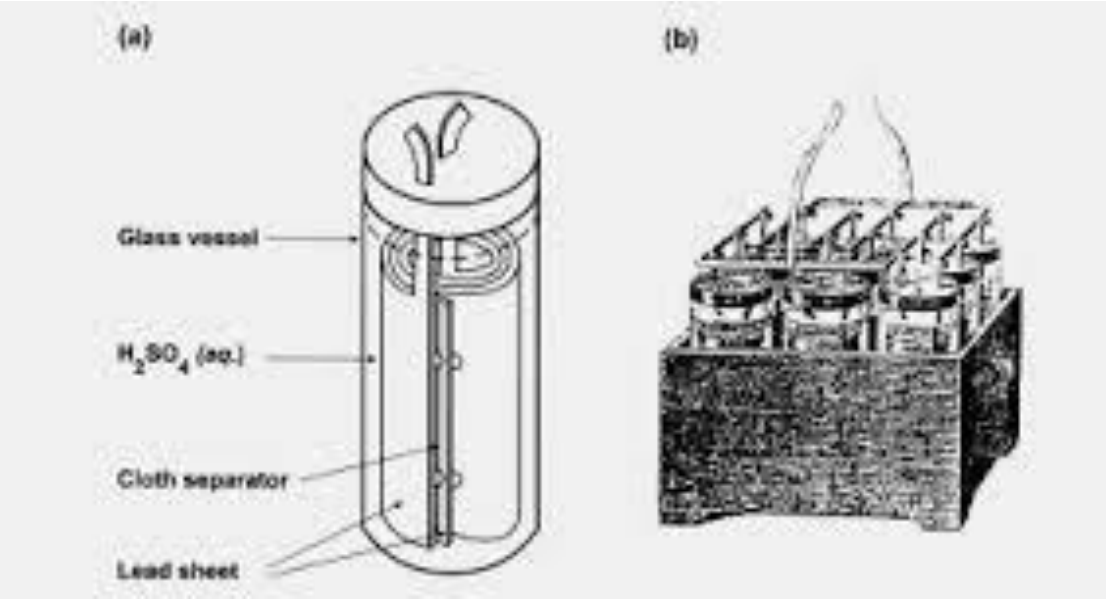


Fig. 2.2 a) Schematic of Plante's Lead-Acid Cell. b) Early illustration of battery with nine cells. (Image Source: www.ciando.com)

Carbon is used in the name of expander in the lead acid battery. The term expander is applied to the mixture of additive materials added to the negative paste either to maintain or enhance the performance of the battery during the operations.

Typically, an expander contains barium sulphate, carbon black, lignosulphonate and other organic or inorganic materials in different proportions suitable for various applications. Early studies on the effects of carbon edition in the negative space showed that carbon functions primarily as a conductor thereby enhancing the formation efficiency and reduces the level of residual sulphate, later it was also observed to improve recharging condition particularly under deep discharges. It was further concluded that when combined with barium sulphate and organic component atypical carbon addition of around point to percentage influence on the discharge performance and cycle life of the batteries for different applications shown in below Fig. 2.4, 2.7 and 2.9.

Masaaki Shiomi et al (1998) estimated the usage of carbon black leads to form a conductive network between the active material to enhance the recharging ability especially in the negative electrode of the lead acid battery.

Ohmae et al (2003) has identified that the conductive carbons are very much necessary for NAM to benefit from the progressive failure (Sulphation). Therefore, addition of conductive carbons will reduce the PbSO4 formed crystals effectively and increase the life cycling ability of the batteries.

Spence et al (2008) presented the improvement in battery performance by using carbon in the NAM. The main beneficial effect of using carbon is, it alters the pore structure of NAM and helps electrolyte interaction effectively with the active material.

Boden, et al (2010) described that the carbon particle is suppressed under the lead sulphates and couldn’t be able to get the benefit by losing it conductive path. With the increasing carbon concentration, he could be able to achieve superior performance. However, the surface area and the structure of the carbon impacts the pore structure of the NAM. It is also noted that with increase in carbon concentration the water loss is evident, this is due to the structural nature of carbon used.

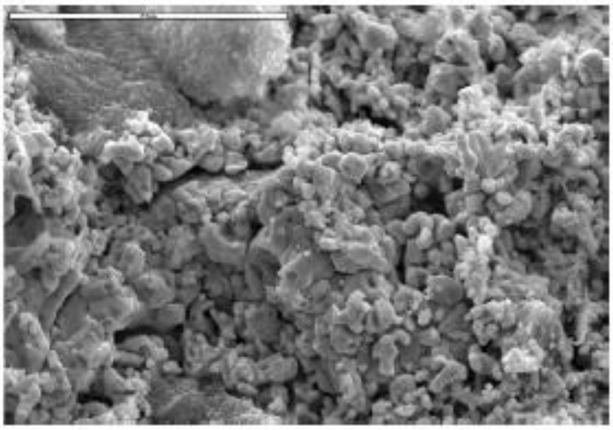
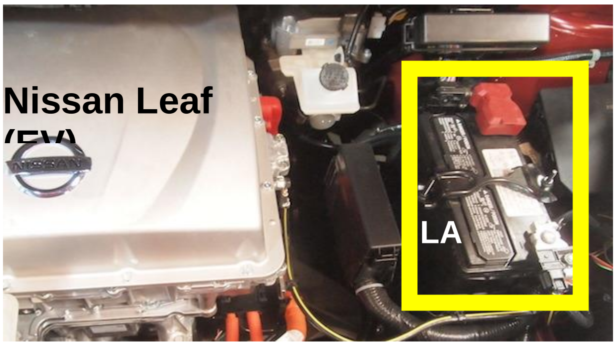


Fig. 2.3 SEM image of Negative plate with Carbon Black after life cycle. Carbon Black particles are completely covered with hard $PbSO_4$ particles. (Scale: 20µ)

Kozawa, et al (1999) explored in a novel way by adding carbon to the electrolyte as an additive. While carbon acts as nucleation site for lead deposition during charging and helps to reduce the sulfation in the NAM.

Pavlov, et al (2011) expressed that by having the carbon would enhance the surface area of the plate. Which keeps the plates in active mode by restricting the sulphates growth in the negative electrode.

Moseley, et al (2018) elucidated the carbon as a capacitive component, by increasing the carbon concentration in the negative electrode, the conductivity path has also increased with improving the battery performance. However, these improvements are compromised with the water loss at higher concentration of high surface area carbons. Particular to Hybrid Electric vehicle application the rapid operation of the battery has sustained with the use of carbon.



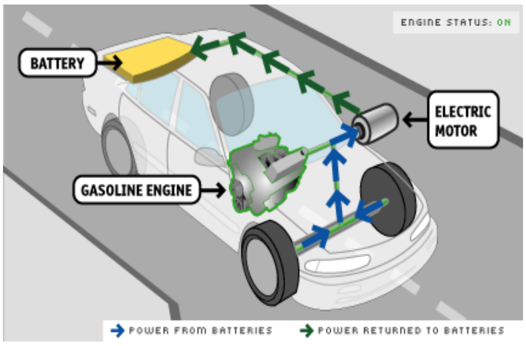


Fig 2.4 Hybrid EV/Regenerative Braking of Nissan Leaf, where Lead acid battery is used as a secondary source.

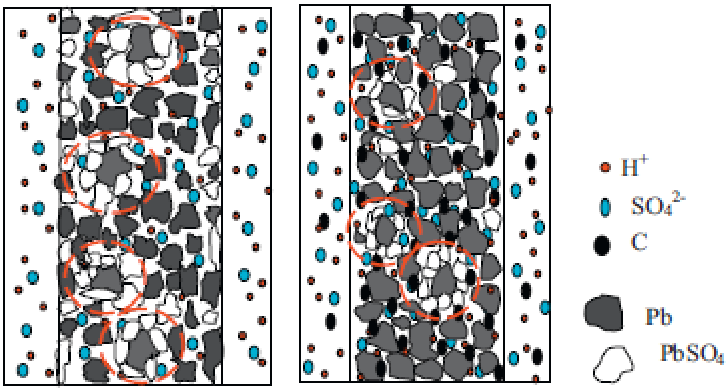


Fig. 2.5 Schematic diagram of effect by without and with carbon additives on negative electrode in operation (X. Zou et al., 2015).

Fernandez, et al (2010) explained about the side effects of using high surface area (>500m²/gm) carbons with higher concentrations. The enhancement in charge acceptance had proved that carbon works as a capacitive component in the lead acid battery. However, the water loss has resulted as a limitation subjected to the form of carbon used. The carbon crating the conductive path has been successful in reducing from the non-convertible $PbSO_4$.

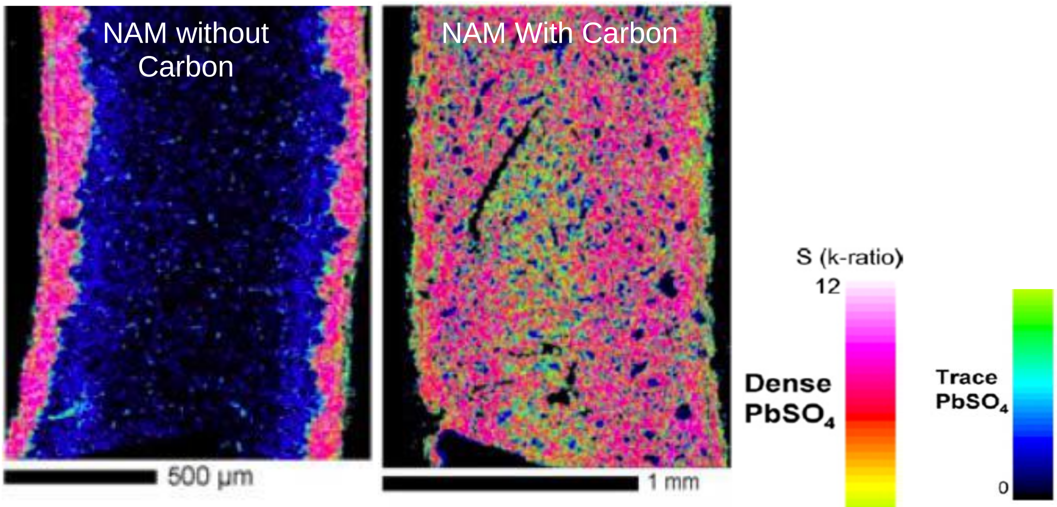


Fig. 2.6 Restricting the formation of hard sulfates by adding carbon in the NAM (Fernandez et al., 2010).

Spence, et al (2009) & Valenciano, et al (2017) also found the optimal use (0.2 - 2% loading w.r.t active material) of graphite flakes in the Negative electrode and improving the battery performances for Ideal Start Stop (ISS) / PSoC application.

Fig 2.7 Ideal Start-Stop/Cranking available in automotive of 4wheel and 2wheel drive.

Jakub Lach et. al., (2019) has developed a novel Pb/C electrode for stationary backup application at high discharge currents. And compared the performance with the regular batteries and found to be recommended, with Pb/C based battery the charging/discharging cycles were able to achieve 275 cycles, almost 2times of the control batteries. However, the construction of the electrode component involves more time than making a conventional battery. This restricted to the laboratory and needs to be worked for commercial scale.

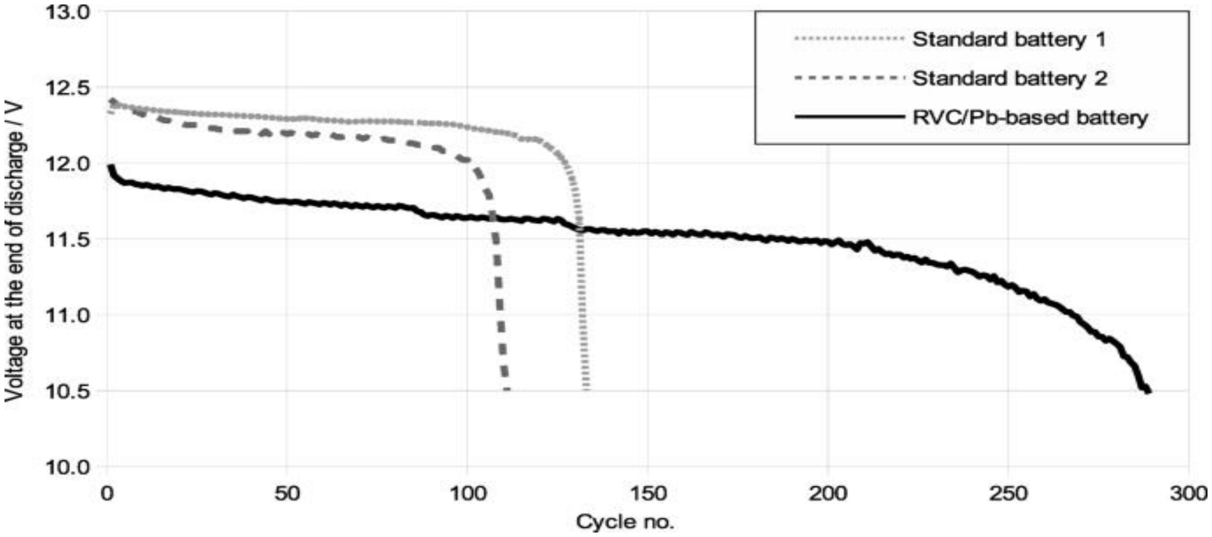


Fig. 2.8 End voltage of failed batteries operated with complete charge/discharge cycles. Jakub Lach et. al., (2019).

Fig 2.9 Telecommunication/Solar Integration of lead acid batteries.

2.4 Application of Carbon in Lead Acid Battery for premature failure

Generally, Lead grids are used for preparing electrodes for lead-acid batteries. The lead grids undergo severe stress under electrochemical operation particularly positive grids. These grids corrode in due course of time causing lower battery performances. This was observed with low antimony (%) and no calcium (%) in the lead alloys. But this corrosion had been addressed by several researchers by adding Tin (Sn) with different concentrations to the lead metal as per the application. But very minimal study has been carried on the development of the resistive layer on the grid/paste interface.

Paul Ruetschi (2005) has explained the development of resistive layer with grid/paste interface and the loss of coherence with positive electrode. Below illustration depicts the transformation of Pb/PbO_2 to $PbSO_4$., which impacts the performance of the battery.

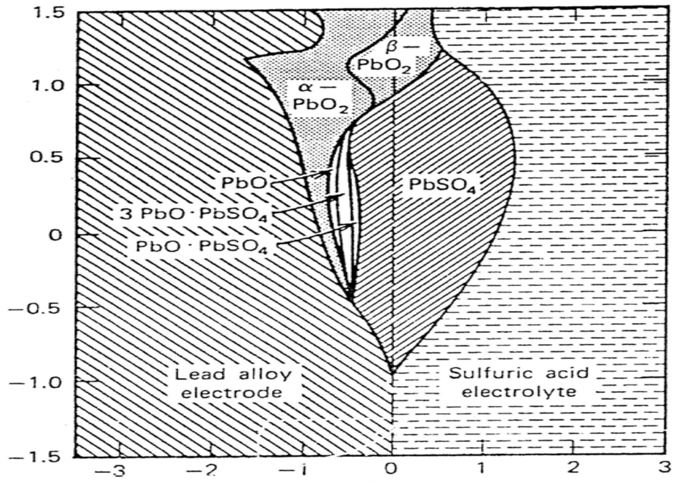


Fig. 2.10 Passivation layer on the positive grid while higher current discharge.

Patent No. CN104362301 (2017), discloses a preparation method for a carbon coated titanium - based lead dioxide positive plate which is obtained by coating a carbon material on the surface of a metallic titanium mesh (instead of Lead mesh) with a vapor deposition method. There are other methods to improve the grid performance in lead - acid batteries. For example, lead - carbon, including lead-graphene and lead-graphite, composites have been tested as possible positive current collectors for lead - acid batteries. It has been shown that neither graphene nor graphite has participated in the electrochemical process but have improved the corrosion and electrochemical behavior of the composite materials.

Few methods employed in the past, as disclosed in **US10388964, 2019** patent, prepared a resin solution with PPCP/ABS (Poly - Propylene Copolymer / acrylonitrile butadiene styrene) as the base material and reinforced with graphene to reduce the resistivity of the resin/polymer and this polymer matrix composite is applied on the grid to act as an insulator. And the patent didn't mention anything about the performances of the battery.

Similarly, in **Patent No. CN103811767, 2018** patent a polymer (PTFE - Polytetrafluorethylene / PVDF -Polyvinylidene fluoride) is used as a binding agent and reinforcing with graphene to increase the mechanical strength and electric conductivity of the grids. In the prior art the graphene material is used a reinforced material into the polymer matrix either to reduce the resistivity or to increase the mechanical strength.

However, the prior art hasn't disclosed about the interface (resistive/sulphate layer) on the positive grid. Employing Polymer/ Resin related binding agent as a precursor or as a base material can be only useful as an insulating material. With polymer (binder/resins) applied on the lead grids also increases the grid weight and influence overall weight of the battery.

M. Saravanan et. al., (2015) attempted to explain the benefit with CNT coated negative grids. His work has explained the successful coating (Fig. 2.11) and the enhancement of grid properties with CNT material and suggested for more investigations, which are needed with other designs and materials to resist the piled-up resistance over the grids.

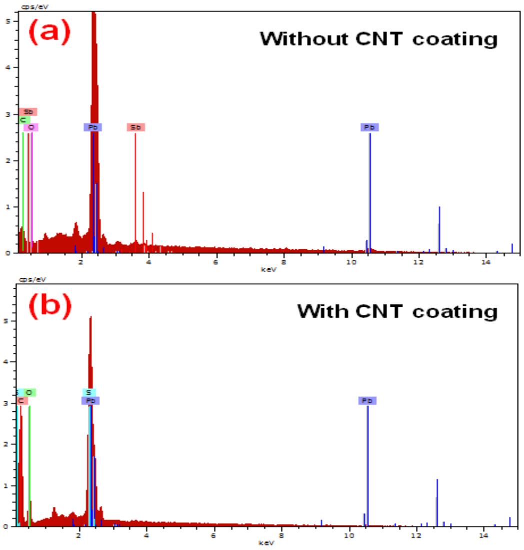


Fig. 2.11 EDX spectra (a) Grid without coating (b) Grid with CNT Coating.

Therefore, there remains a challenge and need to address development of the sulphate/resistive film on the positive grid/paste interface to overcome the drawbacks of the prior arts.

2.5 Gaps Identified

a) Synthesis of Graphene (2D- Carbon)

The technologies that move forward our modern society such as automobiles, airplanes, lasers, and portable electronics et al, rely on the carbon-based materials which could supply energy continuously. A facile and novel route of preparing graphene material would be the prime focus. The desired material should have stable structural properties and must be helpful in applying to the energy storage applications. Low dimensional carbons have always been in the limelight for studying in a wide range of fields. For example, CNT's and graphene are emerging as next generation materials with high mechanical and thermal properties.

Graphene with adequate surface area and pore structure would show great promise in the applications such as batteries, supercapacitors, and fuel cells.

b) Graphene for Lead Acid Energy Storages

Since the allotropes and forms of Graphitic carbons was established as electrochemical intercalated material for the battery application. Intercalation/deintercalation of hydrogen and sulfate ions, in and out of the porous active material upon cycling forms the requirement of carbon as the most suitable anode of the battery. Carbon, thereafter, becomes the preferred additive for negative active material due to its good cyclability, better charge acceptance and high current discharge characteristics. To date, amorphous carbon black is the most widely used form of carbon in NAM of LAB. Therefore, crystalline carbons like graphene need to be developed towards a higher capacitance and better stability. Generally, carbon materials are used in powder form as an additive in NAM. Now the approach of applying must go beyond the NAM, to get the maximum benefit out of it.

2.6 Summary

In this chapter few conventional graphene synthesis methods are being examined along with an improved and novel approaches. The best suited existing method or by modified method will be adapted to produce graphene in a meek and tranquil manner. Further Graphene is made use as an additive along with $BaSO_4$ & Lignin for negative electrode of lead acid energy storages and will be tested.

Three major areas need to address for the performance improvement of Lead Acid batteries.

a) Synthesis of 2D-Graphene.

b) Development of graphene colloidal solution for coating the lead grids.

c) Preparation of Negative electrode with graphene as an additive.

Above to these areas, developing high-performance electrodes and devices should follow the below criteria:

1) Active interface between grid and the active material.

2) Electrically conductive pathway in the NAM.

3) Mechanically stable electrode to sustain the vibrations caused in the field operation.

To achieve the criteria mentioned above, the design of high-performance carbons is supposed to follow these directions:

a) Well-defined carbon structure and pore configuration.

To achieve a high energy/power density, LAB requires the carbon to efficiently intercalate Hydrogen and Sulphate ions on to the electrode surface to accumulate as much as possible, thus a large surface area and approachable surface/bulk interiors is desired when designing and synthesizing carbons. From another aspect, to obtain a high-power density, the carbons are demanded to transport ions and electrons efficiently. Therefore, a good conductive framework including interconnected pores and appropriate pore size are desired.

b) Electrochemically active and stable interface

All the chemical reactions take place at the interfaces of Electrode - Electrolyte and Grid - Active material. Hence, foremost, the carbons should be well approached and infiltrative by electrolyte. The hydrophobic/hydrophilic properties are influenced by the nature of carbon materials, carbon surface functionalities, and carbon surface charge properties. Moreover, during the electrochemical charging/discharging process, carbon should be chemically/mechanically stable in electrolyte in the given electronic conditions. The carbon with less/no side reactions, tolerant voltage/current ranges, and robust frameworks are desired to achieve this goal.

CHAPTER – 3
PROBLEM DEFINITION

In the previous chapter a brief explanation about the preparation of Carbon/Graphene and its applications in lead acid battery were discussed with possible areas for future research. Further there is much scope in developing the advance lead acid batteries with graphene material. In this chapter we will identify the areas hindering the performance of the battery the failures related to lead acid battery.

3.1 Statement of The Problem

To enhance the performance of lead acid energy storage like the initial discharge capacity / energy density, charge acceptance, high current discharges, and cycle life. The material studies need to be carried out, to provide better understanding of the material properties. Taking forward with electrode preparations to enhance the electrical properties of the lead grid and the active material of the battery. To achieve this goal, graphene material is explored as an additive material in the electrode preparation to enhance the electrical performances of the proposed research. In below we will discuss about the failures associated with lead acid battery.

3.2 Reasons effecting Lead Acid battery performance

The reasons mentioned below are categorized as per the device fabrication and operation.

a) Catastrophic Failure (CTF)

b) Premature Failure (PMF)

c) Progressive Failure (PGF)

a) Catastrophic Failure (CTF)

This results, either from manufacturing perspective or from the operational conditions at the time of preparing the energy storage devices.

1. Mismatch of the component selection (+Ve/-Ve electrodes)
2. Poor manufacturing quality (Interconnections/defect separators etc.,)
3. Under charging & Over charging of the device
4. Internal or external damage of the cells (Terminal leakages / Heat seal of PPCP material)

The above issues can be addressed and fixed by controlling the process parameters & manufacturing feasibility with quality controls.

b) Premature Failure (PMF)

Based on the electrical characteristics of lead acid energy storage the main reason of premature failure, is the loss observed at deep discharges of the lead alloys with the development of a high resistance film between the lead grid and the active material (Grid/Active Material Interface) shown in the fig. 3.1, when operated in Over/partial charging / Idle condition. Even at the time of active material pasting process (electrode preparation) sulphate/resistive layer is developed due to the interaction of H_2SO_4 available in the paste. But, at the operations providing a constant/abnormal charge voltage, will increases the development of passivation layer on the grid and could not be able to perform at high current discharges with required capacity.

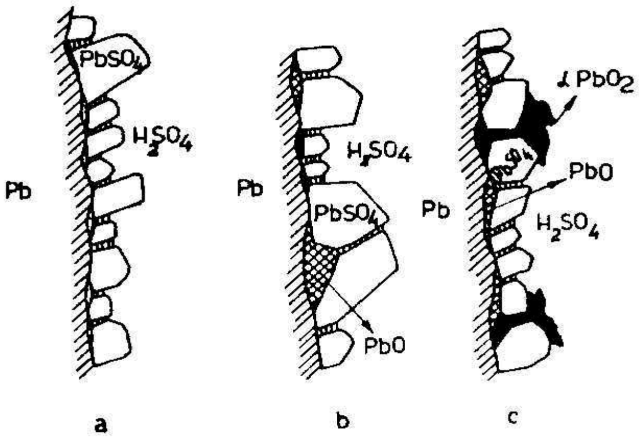
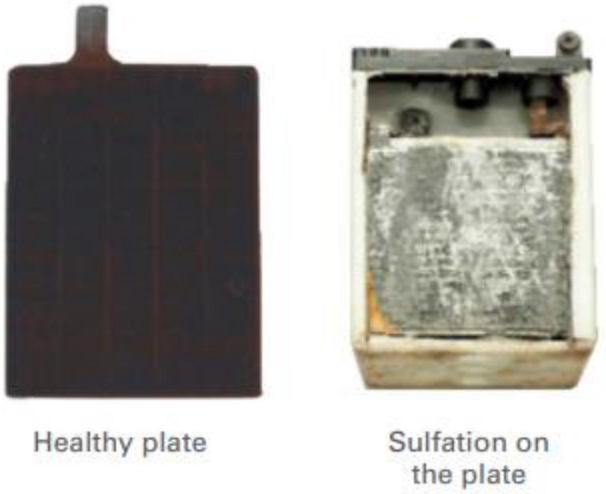


Fig. 3.1 Step wise formation of Passivation/Resistive layer on the lead grid. (This interface hinders the performances of the battery by resisting the flow of current)

c) Progressive Failure (PGF)

Progressive failure (PGF) happens with the active material of the negative electrode. As gradual growth of sulphation occurs at the negative electrode of the battery when subjected to higher number of cycles of charging & discharging or prolonged storage. A complete discharge battery will allow the sulphation (PbSO4) to pileup as shown in fig. 3.2. The application associated with this process are Hybrid/Full EV, PSoC and HRPSoC conditions. This sulfation will also affect the Initial discharge/Energy density, charge acceptance and High current discharge abilities. These sulphated crystals would increase the resistance of the electrode, which wouldn't be reconverted back to metallic lead. This would also require large currents to dissolve these sulphate crystals but would not be successful due to the lack of conductive path in the electrode, which are suppressed by the sulphates. In will also form dendrites on the electrode/separator interface, causing short circuits of the electrodes and permanently damaging the battery.



Healthy plate

Sulfation on the plate

Fig. 3.2 Formation of Sulphation on the negative electrode over a period.

The specific purpose of this proposed research is to enhance the performance of lead acid energy storages by addressing PMF and PGF. The performance enhancement can be analyzed with the parameters such as high current discharges, charge acceptance, Initial discharge capacity/energy density and life of the device.

3.3 Our Approach for Possible Solutions

1. For PMF, lead grids are coated with prepared Graphene/Carbon colloidal Solution to limit the formation of passivation layer on the grids.
2. For PGF, Graphene/Carbon is added as an additive to inhibit sulphation in Negative active material.

3.4 Experimental Approach for Premature Failure (PMF)

Step 1: Graphene Colloidal Solution Preparation.

Step 2: Coating the grids with graphene solution on the lead grids.

Step 3: Evaluation of coated electrodes.

3.5 Experimental Approach for Progressive Failure (PGF)

Step 1: Negative Electrode preparation with Graphene as an additive in the active material. The advantage of having Graphene in the active material is illustrated in Fig. 3.3.

Step 2: Evaluation of assembled graphene aided electrodes as a device.

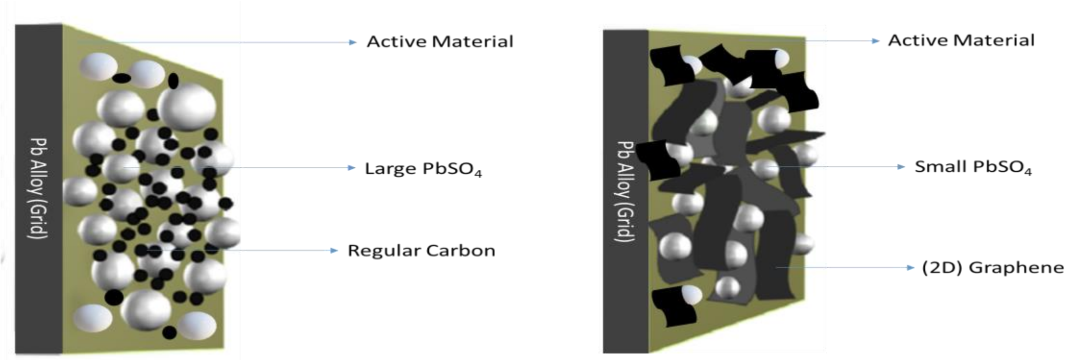


Fig 3.3 Mechanism of graphene in active material

Herein, this proposal presents a facile synthesis route of graphene preparation to achieve a unique property with high productivity. There are several advantages and disadvantages of synthesizing 2D-Carbons/ Graphene material in each way. Graphene prepared by Chemical Vapor deposition (CVD) or mechanically exfoliated technique have the purest with less defects. It holds the properties near to the theoretical values. But the cost with these techniques is high and the rate of production is less which is not a cost-effective approach. Whereas other methods involving chemicals like hummers method can produce graphene in large scale but lacks in purity (more defects and presence of other functional groups). So, there is a need for a better method with reasonable purity and productivity. In this work few synthesis methods presently in use are examined along with an improved and novel approach to prepare graphene by simple means. The prepared graphene is taken forward to address Premature Failure (PMF) and Progressive Failure (PGF) as a coating material on to the grids and as an additive in active material of negative electrode for lead acid energy storages. The electrochemical measurements are carried out in standard sulfuric acid as an electrolyte for both the approaches.

3.5 Summary

From the previous chapters we have been able to Identify the areas for improving the battery performances like Charge acceptance, Initial Discharge Capacity/Energy density, High current discharges. PMF & PGF, are within our scope, which affects the performances of the battery. To address the above said failures, graphene material has been chosen, due to its unique electrical properties. Application of graphene material in colloidal phase for targeting PMF. And the same has been applied as an additive to the Negative active material for limiting the PGF.

Chapter 4
Nanomaterial Synthesis

From the previous chapters we understood how crucial the preparation of graphene is. In this chapter we will be preparing the graphene material in a facile and cost-effective way. And we also characterize the prepared graphene material with Microscopic, spectroscopic etc., related qualitative tools.

As we discussed about graphene in earlier chapters, as a promising material which can be used in many fields (electronics devices, gas sensors etc.). But to use any material for commercial application there should be an industry level cost effective synthesis method. In this chapter few synthesis methods are presented to corelate and examined along with an improved and novel approach.

4.1 Synthesis of Carbon Nanomaterials- Existing Methods

- Mechanical Exfoliation (Scotch Tape)
- Chemical Vapor Deposition
- Hummers Method
- Liquid Phase Exfoliation

4.1.1 Mechanical Exfoliation (Scotch Tape)

In year 2004, Nobel Prize has been awarded for the discovery of 2-Dimensional carbon, which is graphene for the physicists Prof. Andre Geim and Prof. Konstantin Novoselov from University of Manchester, UK. They have used a scotch tape to extract graphene from the graphite and were successful in pulling out few layers of graphene, which later examined under an optical microscope (Fig. 4.1) categorized by light absorption.

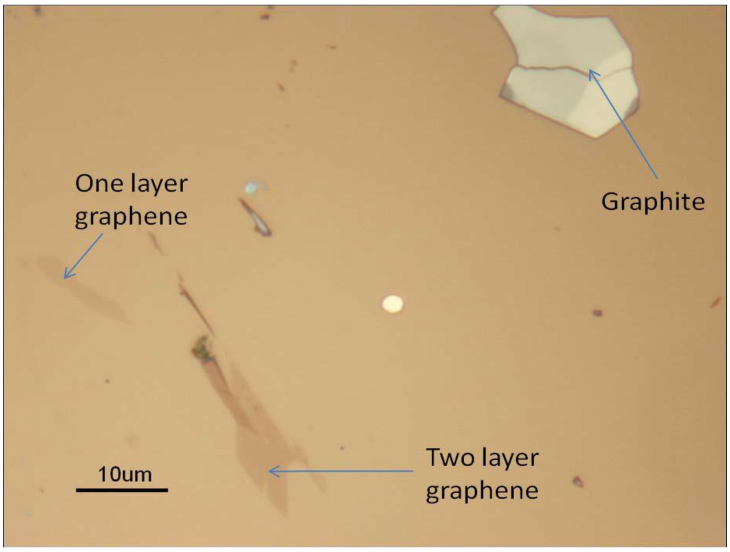


Fig. 4.1 Mechanically exfoliated graphene on SiO_2 imaged with white light using an optical microscope (Photo credit: Nathaniel Safron).

4.1.2 Chemical Vapor Deposition (CVD)

CVD process is a way of thin film technique where the atomic deposition takes place by the gas molecules (Hydrocarbons - CH_4) as a precursor onto a substrate in layered manner. The rate of deposition, number of layers and thickness of the material can be altered according to our requirements. Several researchers have synthesized with this technique with different temperatures and environmental conditions created in the chamber (Low Pressure CVD, Plasma enhanced CVD, Ultra-High Vacuum CVD etc.,). The process involved with CVD is shown in Fig. 4.2. The benefit with this deposition process is that we achieve in high purity graphene layers, but with low quantity. The other disadvantages with are process is the by products like Carbon Monoxide (CO) which need to be disposed carefully. This method would be more viable for making semiconductors to carryout lithographic steps and related optoelectronics industries.

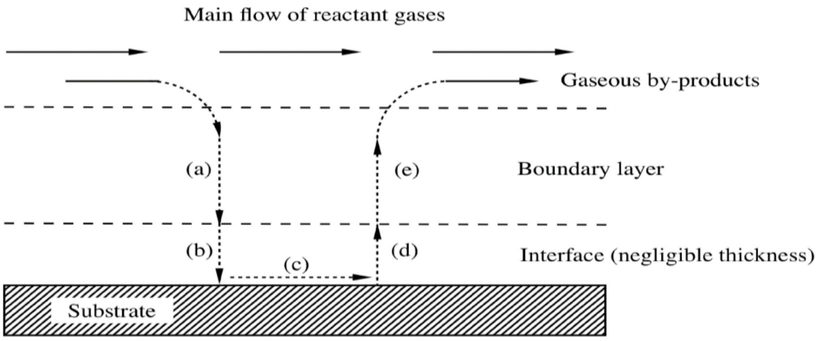
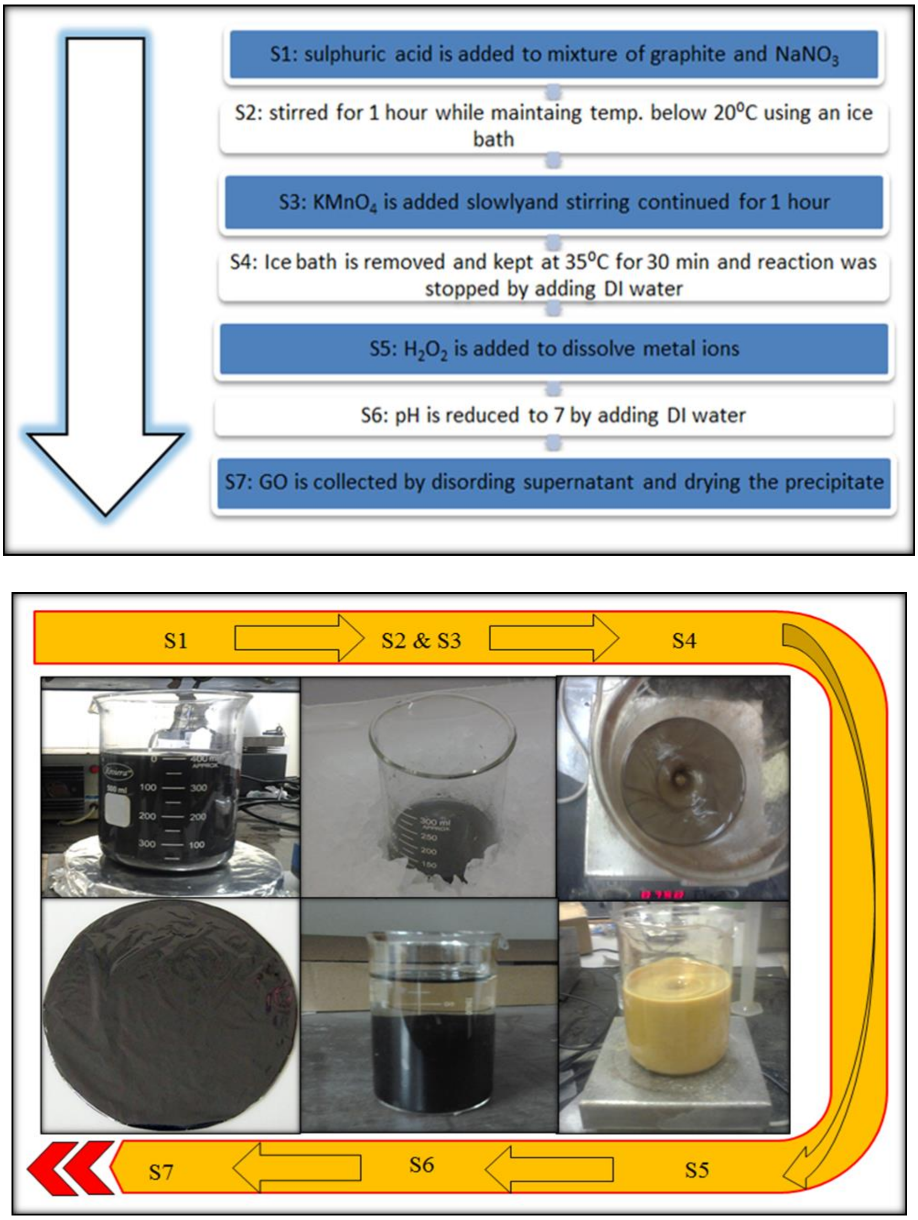


Fig. 4.2 Steps involved by CVD process:
(a) Diffusion in process of hydrocarbons (reactant gas).
(b) Atomic adsorption (Carbon) with the substrate.
(c) Chemical reactions on the substrate.
(d) Desorption of unabsorbed carbons.
(e) Diffusion out process of unabsorbed carbons and by-products.

4.1.3 Hummers method

2:1 ratio of graphite flakes (3gms) and sodium nitrate (1.5gms) is well mixed and Conc. Sulfuric acid (70ml) is added to the mixture and placed in an ice bath to restrict the temperature growth. Later $KMnO_4$ (6gms) is added and stirred by maintaining the temperature under 20°C. After removing ice bath, the mixture was stirred at 35°C for 30 min. The mixture started becoming thick after 20 min of stirring. A very thick paste was formed after 30 min. DI water (138 ml) was added slowly to the thick paste and stirred to stop the reaction. After 15 mins further addition of water (450ml) to the solution is added to completely stop the reaction and stirred for 30 mins. Later, Hydrogen Peroxide (H_2O_2) with 30% concentration is added 5 ml to reduce metal oxide particles, to wash out easily with water. Change in the color of the solution from reddish brown to brilliant yellow is an indication of reduction of metals in the solution. After reduction of metals, the solution is washed and filtered, later allowed to dry at 105°C for 24Hrs. The dried-out material is the graphene with few layered structures. The whole process takes time about 2days and involves exothermic and violent chemicals.



S1: sulphuric acid is added to mixture of graphite and $NaNO_3$

S2: stirred for 1 hour while maintaing temp. below 20°C using an ice bath

S3: $KMnO_4$ is added slowlyand stirring continued for 1 hour

S4: Ice bath is removed and kept at 35°C for 30 min and reaction was stopped by adding DI water

S5: H_2O_2 is added to dissolve metal ions

S6: pH is reduced to 7 by adding DI water

S7: GO is collected by disording supernatant and drying the precipitate

Fig. 4.3 Synthesis of graphene oxide using hummer's method (Top) Flowchart and (Bottom) experimental pictures

4.1.4 Liquid phase exfoliation

Graphene can be produced directly from graphite using this method. The energy required to separate graphite layers will be produced from the interactions of graphite surface and the solvent used. This process is possible only with few organic solvents like NMP (N-Methyl-2-pyrrolidone), DMF (Dimethylformamide) etc.

Graphite (50mg) is added to DMF (250ml) and sonicated for 2 hours using ultra probe sonication. Sonication can be continued until a clear solution is formed and there should be no agglomeration at the bottom or on the top. The solvent is made evaporated, and the resultant powder is collected after properly drying in hot air Owen for 2hours.

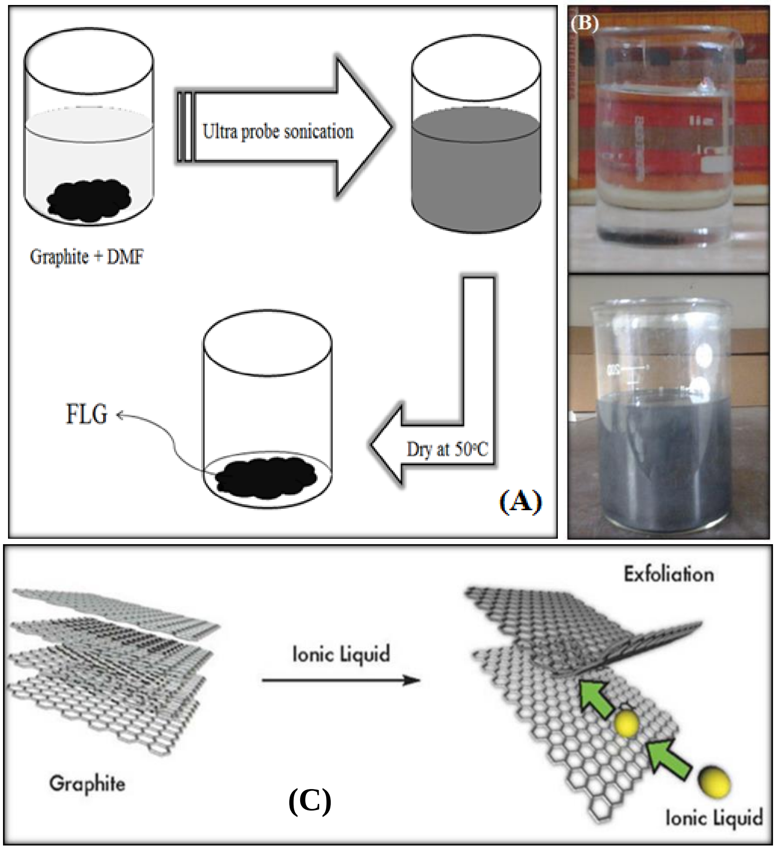


Fig. 4.4 LPE (A) Schematic diagram and (B) Experimental pictures and (C) Graphical representation.

4.2 Our Approach: Microwave Irradiation (Novelty in this work)

In this work graphite is intercalated with oxygen functional groups using aqua regime (3:1). Graphene oxide can be reduced by supplying enough energy in any form (thermal, microwave radiation, solar radiation etc.). When energy is applied water molecules and oxygen groups tries to escape (evaporate) from GO. In this process they break the bonds between individual layers and separate them to form reduced graphene oxide. We cannot remove oxygen groups completely, but after some point it will be stable and holds similar properties to that of pristine graphene. This process is explained below in detail. Materials used in this work: graphite flakes (150 μm) (Sigma Aldrich). Sulfuric acid (98%), Nitric acid (70%), hydrochloric acid and Hydrogen peroxide were purchased from Merck.

In a beaker of 1 liter, 400ml of acid mixture (aqua regime) in a known ratio was taken and 3g graphite was added to it. It was then stirred for a known time. The reaction was then stopped, and the suspension was allowed to settle down. The clear solution or the acid mixture (supernatant) is then decanted through which roughly 75% of the acid was removed. Dilution with DI water and removal of supernatant was repeated until the pH reduces to 7. It was then dried at 50°C in Owen for 8 hours. Remaining solid is collected and stored. We call it acid treated graphite (ATGF). Microwave treatment of above prepared acid treated graphite expands and becomes less dense as the inter planar distance between the graphite layers increases. This expanded ATG is called graphene warms (GW). Graphene warms are dispersed in ethanol in 0.05 mg /10 ml ratio and sonication is done for 30 minutes using ultra probe sonication. A stable colloidal dispersion is formed, which then dried to collect the remaining solid product.

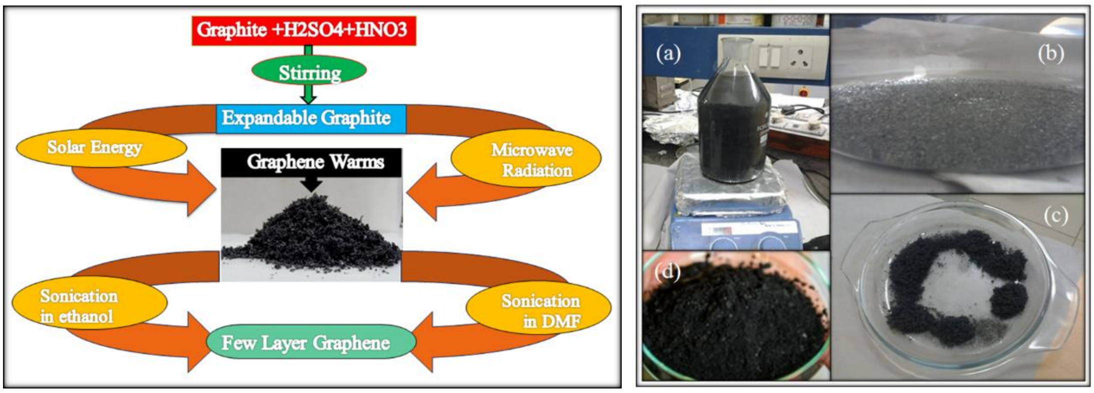


Figure 4.5 Optimized novel approach used in this work (A) Flowchart (B) Experimental pictures (a) Acid treatment (b) ATGF (c) MWGW (d) MWG

4.3 Summary

Various methods for synthesizing graphene were studied and initiated novel approach to synthesis graphene in environmentally friendly way with cost effectiveness. Initially using aqua regime graphite was partially oxidized which then exposed to microwave radiation to get graphene worms. By sonicating these worms in ethanol environment until the formation of a uniform solution is achieved followed by evaporation of solvent to collect Graphene material. Instead of exposing acid treated graphite flakes to microwave radiation we can also use other means (Thermal & Solar) to produce graphene which is safe and freely available. Use of other energy sources to realize further effective and cheaper method is continuation and future aspects of this work.

Lack of bulk production of mono layered graphene by chemical routes is a major stumbling block related to this research. Graphene produced from the above said process, would not be much useful in semiconductor related industries producing IC's/ Transistors etc. But the graphene material obtained from the above said process is quite compatible for energy storage industries. The material characterization and application of graphene in lead acid energy storages will be discussed in next chapters.

Chapter 5
Material Characterization

In the above chapter, we have discussed about the synthesis of graphene material. Now we will discuss the qualitative analysis of the synthesized graphene with different characterization techniques. And the summary is drawn about the successful synthesis of the desired material, which will be applied to making lead-acid energy storage device.

The morphological studies were carried out by using Scanning Electron Microscope (SEM) model 6010Plus/LV of Jeol-USA and Transmission Electron Microscope (TEM) model FEI Tecnai G2 S-Twin. XRD experiments were carried out using Rigaku Ultima IV, Japan.

The Raman Analysis were carried out with Nd-YAG laser source of WiTec, Germany. XRD and Raman studies were used to understand the structural revelation and then to correlate with morphological observations. Resistance calculations are made using 2-probe method. Surface area measurement of the prepared graphene materials were carried out by Coulter, model 3100, USA.

5.1 Scanning electron microscopy

A SEM is used to study morphology of nanomaterials completely or in part. Electrons generated from an electron gun are accelerated using high electric field and directed towards specimen. During the passage through vacuum primary electrons will be focused by electric field to form a narrow monochromatic beam which hits the specimen and liberates secondary electrons. Secondary electrons liberation depends on angle and velocity at which electron beam is hitting. This signal is amplified and transformed to a video scan-image that can be seen on a display that can be saved and processed further.

Electron micrographs of the graphite flakes (starting material) and graphene are observed from the images that the graphite flakes are thick and stacked type structure (in the order of few µm) as shown in Figure 5.1. The randomly aggregated thin graphene sheets (few of them stacked together forming independent FLG structures) closely associated with each other and forming a disordered solid. The folded regions of the FLG sheets are found to have an average thickness of few nm. The absence of charging during the imaging indicated that the material was constituted with a network of graphene-based sheets that are electrically conductive. It can also be observed from Fig. 5.1 that FLG sheets have lateral dimensions of at least 1 µm2. Fig. 5.1 is the evidence that the adopted method (i.e., oxidation of graphite flakes followed by microwave irradiation and subsequent probe sonication) is an optimum one to convert very large number of stacked graphene layers in a cost-effective way.

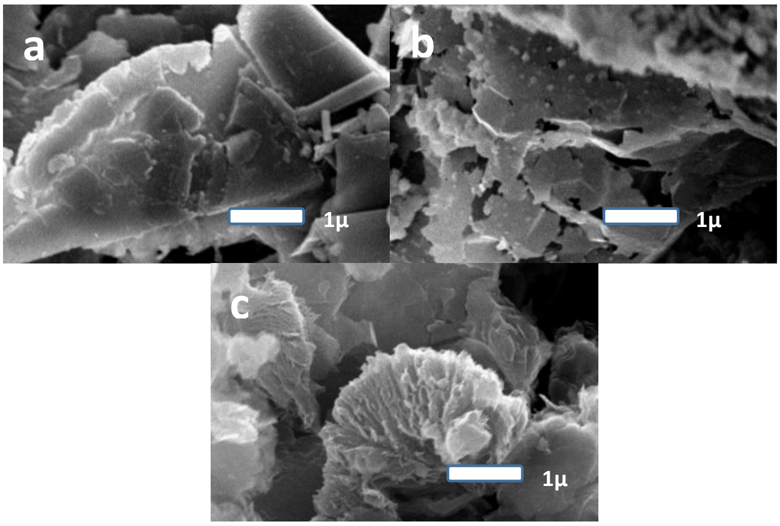


Fig. 5.1 Secondary electron micrographs of
(A) graphite flakes and (B) Expanded Graphite (C) Graphene

5.2 Transmission Electron Microscope (TEM)

Wide beam of electrons generated using an electron gun are accelerated towards a thin specimen to form an image. Working principle of TEM is analogous to a standard microscope. Very thin specimen (sample) is used as the electrons need to penetrate through it. Electrons generated by electron gun are made to travel through the thin sample placed in the middle of the equipment of which some are penetrated, absorbed, and reflected. The sample is placed in the middle of the equipment to capture the black and white image on the screen placed at the bottom.

5.2.1 Sample preparation for TEM

Graphene is added to ethanol (0.1mg/10ml) and sonicated to get a clear solution. Using a micro pipette, a drop of it is transferred onto TEM grid and let it evaporate. This grid with sample coated as a film is used for TEM studies.

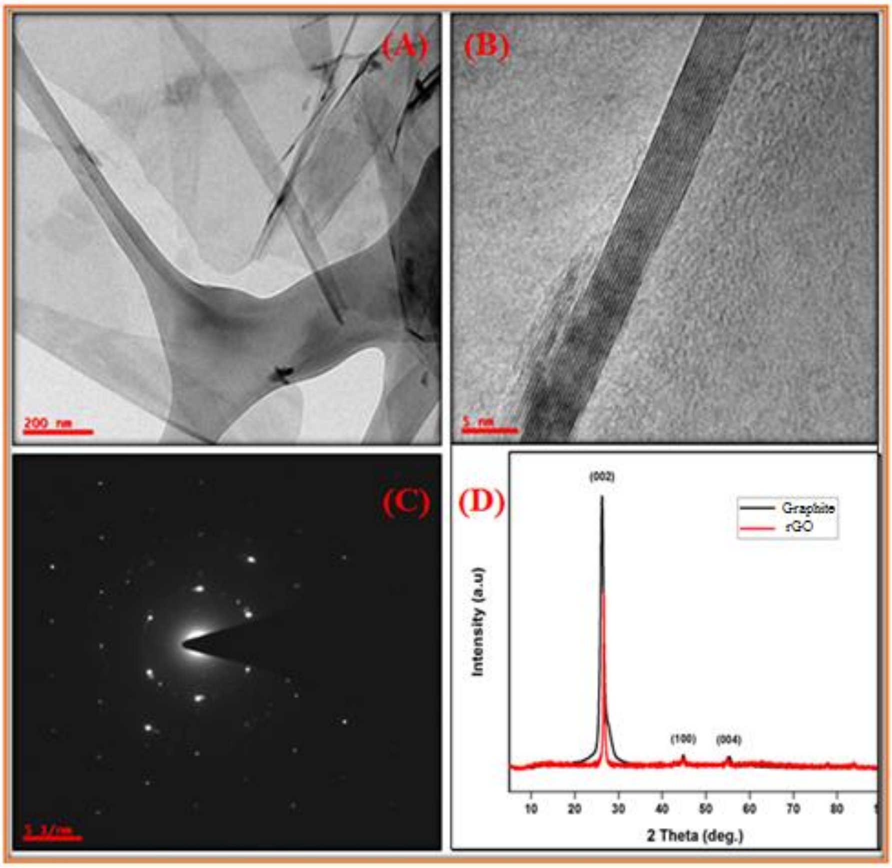


Fig. 5.2 (A) Transmission electron micrograph of few layered graphene, (B) corresponding planar view, (C) corresponding SAED pattern and (D) comparison of x-ray diffractograms of graphite and FLG

The above mentioned FLG sheets are transparent to the electron beam as observed in transmission electron micrographs (Figure 5.2(A)) indicating the presence of few layers along the c-axis in a single structure. Comparison of x-ray diffraction data obtained from FLG with graphite (Figure 5.2(C)) showed a typical (002) and (004) with reduced intensity indicating the formation of graphene through exfoliation. The x-ray diffractogram obtained from FLG also indicated that it is highly ordered.

Figure 5.2(B) showed the typical sixfold symmetry as expected for Selective Area Electron Diffraction (SAED) pattern of FLG. This is complemented well with that of XRD data. The regular outer and inner hexagon patterns with varied intensity of the electron diffraction spots as shown in Figure 5.2(B) indicate few layers system that is built-in with A-B type of atomic stacking as in graphite.

5.3 X-Ray diffraction

X-ray diffraction is a unique tool of constructive interference to characterize the chemical composition and the crystallographic structures of the material. In general, interatomic spacing of crystals is around 2 to 3 A^0 so the X-rays are the most suitable to study the properties of materials. In works based on the Bragg's law.

$$n\lambda = 2d\sin\theta \qquad \text{-- (1)}$$

Where,

d = Atomic layer spacing; θ = Incident angle; n = Order of reflection;

λ = wavelength of the beam.

X-ray diffracted graphs of all the processed graphite are showed in Figure 5.3. The sharp diffraction (peak) of 002 plane is an indication of stacked layers in few layers graphene.

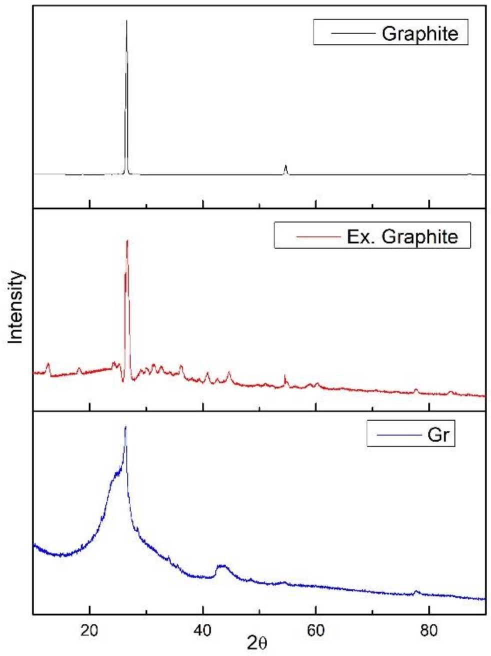


Fig. 5.3 XRD pattern comparisons

Figure 5.3 compares X-ray diffraction pattern of all the intermediate products in the synthesis of FLG from graphite flakes. Diffraction pattern shifts very slightly during this process. Table 5.1 gives the characteristics (full width half maximum and d-spacing) of all materials from graphite flakes to FLG.

5.4 Raman spectroscopy

Raman spectroscopy is very much helpful to study carbon materials purity. The principle is that when a sample is subjected to the monochromatic light beam, the sample absorbs the photons and experiences an inelastic scattering and then re-emits photons. The frequency of absorbed and re-emitted photons is captured, this is called 'The Raman Effect'. The captured frequencies give us the information of the materials vibrational, rotational, and transitional energies of the molecules present in the material.

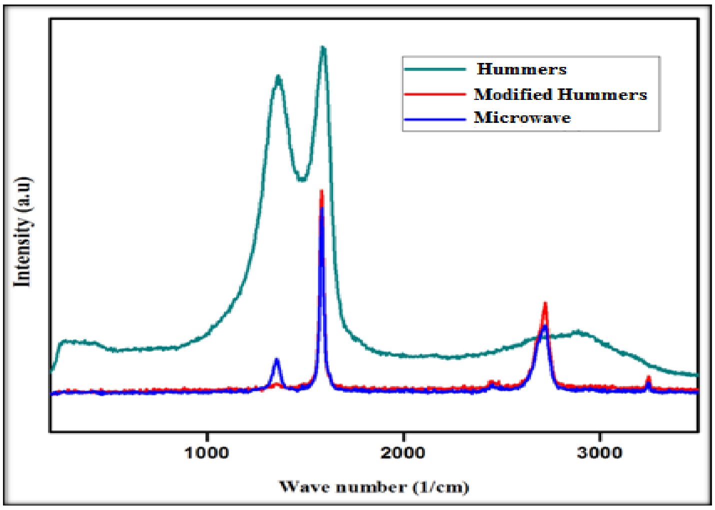


Figure 5.4 Raman spectrographs comparisons

S.No	Method	Graphite (g)	Solvent/acids	Graphene	
				Yield	purity
1	Hummers method	1	23ml	0.3g	poor
2	Improved Hummers method	1	50ml	0.5g	good
3	Microwave	1	100ml + 33ml	0.65g	good

Table 5.1 Comparison among the three synthesis methods

Table 5.1 compares the three methods in different aspects like productivity, purity, cost effectiveness is given below. From these comparisons it is evident that the graphene produced using the novel approach optimized in this work is comparatively better in terms of purity, cost effectiveness, productivity, and conductivity. Especially high productivity makes it an attractive method to synthesis graphene commercially.

Figure 5.4 compares the Raman spectrographs of the three graphene's. Hummer's graphene is having high intensity d band at around 1350cm^{-1} is an indication of presence of defects in graphene planar structure. Reasons for defects may include impurities like oxygen groups or simply the absence of carbon atoms. Unlike in hummers method there will be no oxygen groups present in graphene network in the microwave graphene which can be backed with less or absence of defect band in microwave graphene. This is the reason for low resistance or high conductivity which will be discussed in below section.

In Graphene material it is know that G and 2D bands in Raman spectrum is observed at ~1590 cm^{-1} and ~2685 cm^{-1} as mentioned in Table 5.1. With the higher graphene layers the G band shift towards lower wavenumber and the 2D band shifts towards higher wavenumber and the shape of the 2D band, deforms from sharp to broad peak.

Table 5.2 Bands and intensities of 2D carbons (graphene) by different routes.

Bands	Hummers	Modified Hummers	Microwave
G band	1585	1585	1581
D band	1352	1349	1344
2D band	2720	2712	2713
ID	229	219	218
IG	440	259	394

I2D	316	224	292
ID/IG	0.52	0.84	0.5
IG/I2D	1.3	1.15	1.34

5.5 Resistance Measurement

Pellets are typically created by compressing an original material to study the resistance of the material as per IS 12178 standards. Usage of pellets instead of powders to study their properties (conductivity and resistance) is much easier. It’s a simple process. Depending on our requirements (dimensions of pellet) the amount of powder required can be calculated using simple calculations. Disc shaped pellets were prepared to study conductivity and resistance. To prepare these types of pellets we need to consider diameter, thickness and density for calculations.

<u>Calculations</u>:

Ohm’s Law:

$$\boldsymbol{V} = \boldsymbol{I} * \boldsymbol{R}$$

$$\boldsymbol{V} = Voltage;\ \boldsymbol{I} = Current$$

Resistance $(\boldsymbol{R})$:

$$\boldsymbol{R} = \frac{\boldsymbol{\rho} * \boldsymbol{T}}{\boldsymbol{A}}$$

$$\boldsymbol{\rho} = Resistivity\ (\Omega * cm);\ \boldsymbol{A} = Area\ (cm^2);\ \boldsymbol{T} = Thickness\ (cm)$$

Conductivity $(\boldsymbol{C})$:

$$\boldsymbol{C} = \frac{\mathbf{1}}{\boldsymbol{\rho}}$$

Resistance is a property of a substance to resist the flow of current in an electrical circuit. Appropriate size was chosen and cleaned properly with acetone or ethanol. Substrate used has a cylindrical hole in the middle which can be closed at one end and after placing powder into it, it can be closed on the other end also. Then mechanical force is applied (we have applied ~2 tones) to get it into disc shape. Graphene and its composites have good binding ability. But to have a real time evaluation these powders were mixed with polyester binder and Lead oxide powder as a pellet. These materials are used in the electrode preparation of lead acid batteries.

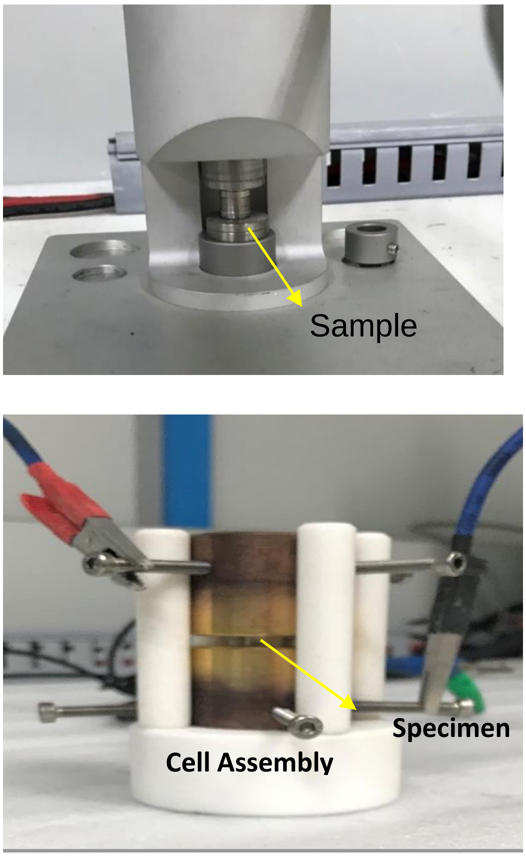


Figure 5.5 In-House development of electrical measurement of the test setup with Sample Preparation and Cell Assembly

5.5.1 Resistance calculation

Resistance is calculated using 2 probe technique. First of all, device is configured, and function is set with Electro-Chemical analyzer (Make: Wonatech, Southkorea). Sample is connected between 2 probes using 2 clips as shown in fig. 5.5. Measurement scans were started, and 04 different values are taken, average of which is taken as the resistance of the material and tabulated below (Table 5.3).

Table 5.3 Resistance Measurement

S.no	Method	Material Resistance (kΩ)
1.	Hummers	0.08
2.	Modified Hummers	0.02
3.	Microwave	0.0025

5.6 Surface Area Measurement

The surface area measurements were carried out with Coulter (3100), USA equipment. Where the Nitrogen (N_2) adsorption technique is followed to measure the surface area of the materials. The prepared graphene material has ~10 times of its original surface area. Table 5.4 discloses the increase in the surface area of the graphite material.

Table 5.4 Surface area measurement using N_2 adsorption.

S. No	**Material**	**Surface Area (m^2/g)**
1	Graphite	11.91
2	Expanded Graphite	16.47
5	Graphene - Microwave	128.99

5.7 Summary

In this chapter, various characterization tools have been used to validate the prepared graphene material. From the microscopic techniques it revealed that few layered graphene is observed. From the XRD spectra we could see the structural changes of graphite, expanded graphite and graphene in the step wise process. By analyzing the sample with Raman spectroscopy, the purity of the microwave is slightly higher with obtained material yield. The resistance of the graphene material is very much lower with the raw material (Graphite). Even the surface area has increased 10 times when compared to that of graphite. Therefore, we can corelate that surface area with the electrical conductivity, which is directly proportional. Now with successful preparation of the graphene material, it is taken forward to prepare the electrode as an additive to the negative active material to address the progressive failure (PGF). And also the same material is used to prepare a colloid suspension for coating the lead grids to address the Premature Failure (PMF) hindering the lead acid battery performances.

Chapter – 6

Experimental Process/Investigations

As we discussed in earlier chapters, in 1860 by Gaston Plante first developed the first practical design of lead-acid battery, since then the production continued to grow. The majority usage of lead acid battery is by Automotive sector then followed by industrial sector like for traction and stand by application. Batteries are the primary customers for the lead producers around the world.

With the low cost and ease of manufacturing ability the lead-acid batteries demand is continuously growing when compared to other electrochemical devices.

The lead-acid battery having a Negative and positive electrode with spongy lead (Pb) and lead dioxide (PbO_2) is prepared with an electrolyte. On discharge, both electrodes convert to lead sulphate. Sulfuric acid solution has been used an electrolyte with the specific gravity of 1.29 (39% by weight). Below sections describes in brief about the components & its process of making a lead acid battery.

6.1 Manufacturing Process: Lead Acid Battery

The below flow chart (figure 6.1) describes the manufacturing process of the lead acid battery. We have followed jar formation in making the device, which involves in less defects, more feasible and ease of machining. These processes are discussed in detailed in below sections.

Device assembly is carried with several components as discussed in Chapter 1. But the real challenge would be preparing coated lead grids and formulating the active material with graphene. This process is called Plate preparation process

(PLP). Followed with stacking with separator into the individual cells of 6 in a plastic container, this is termed as called components assembly process. Later these batteries are sent to acid filling process with desired specific gravity and sent to formation. Once this formation is completed, these are sent to finishing. With ensuring the electrical parameters the devices are ready for installation.

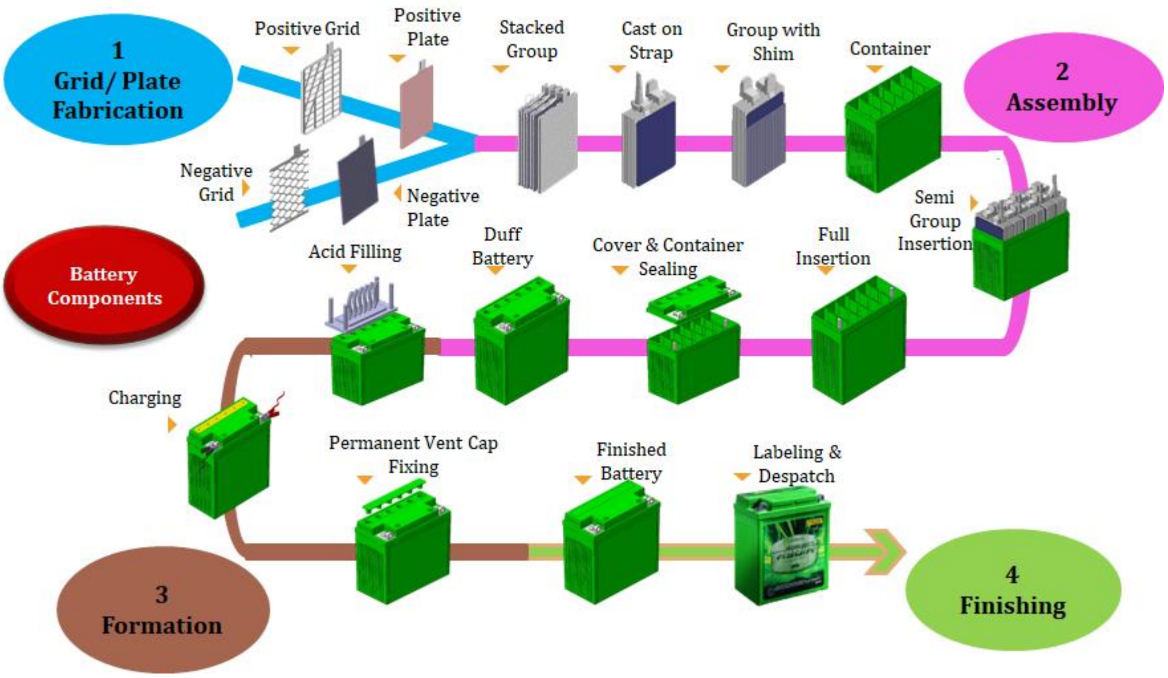


Fig. 6.1. Lead-acid battery manufacturing process.

6.1.1 Electrode Preparation

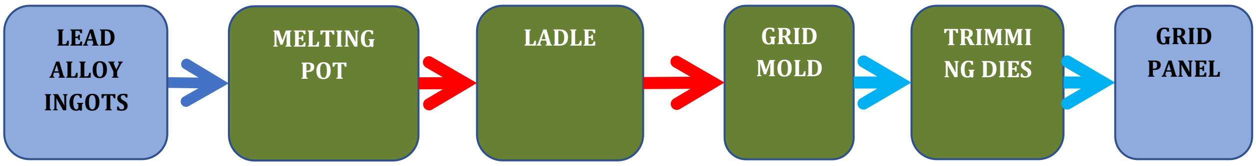
Preparing Positive & Negative Electrode consists of lead alloy as current collector and paste made up of lead oxide and additives vary for positive & negative.

One of the key roles of the battery performance are depends upon its electrode that is battery plate. The good quality battery plate with consistent quality in every lot having much and more demands in the market selection. of blade alloy or casting upgrade within lead acid batteries the importance of positive electrode controls performance songs battery failures is generally caused by degradation of positive plate hey pause 2 grids in all batteries act as both support structure and electrical conductor they must be capable of actions during production pause 2 grades are made from to hold the paste.

6.1.1.1 Lead Grid Preparation:

Fig. 6.2 Lead Ingots for grid fabrication

Through Gravity casting the lead grids are manufactured. Firstly, melting the lead ingots and pouring into the dye of our patented design as shown in below flow.



Gravity casting is the oldest process adopted by battery industry and invented in the year 1931 by Arthur D. Lund. It involves the pouring of molten alloy into mold with a gravitational force as shown in Fig. 6.3.

Fig. 6.3 Gravity casted regular lead grids.

This approach has few advantages, which are listed below.

- Cost effective
- Simple manufacturing process
- Quick solidification
- Uniform grid cooling

Our goal is to address the PMF and increase the battery performance, it is very much needed to prepare graphene solution to coat the lead grids. As the carbon cannot be coated with electro deposition technique, we choose to immersion/dip coating.

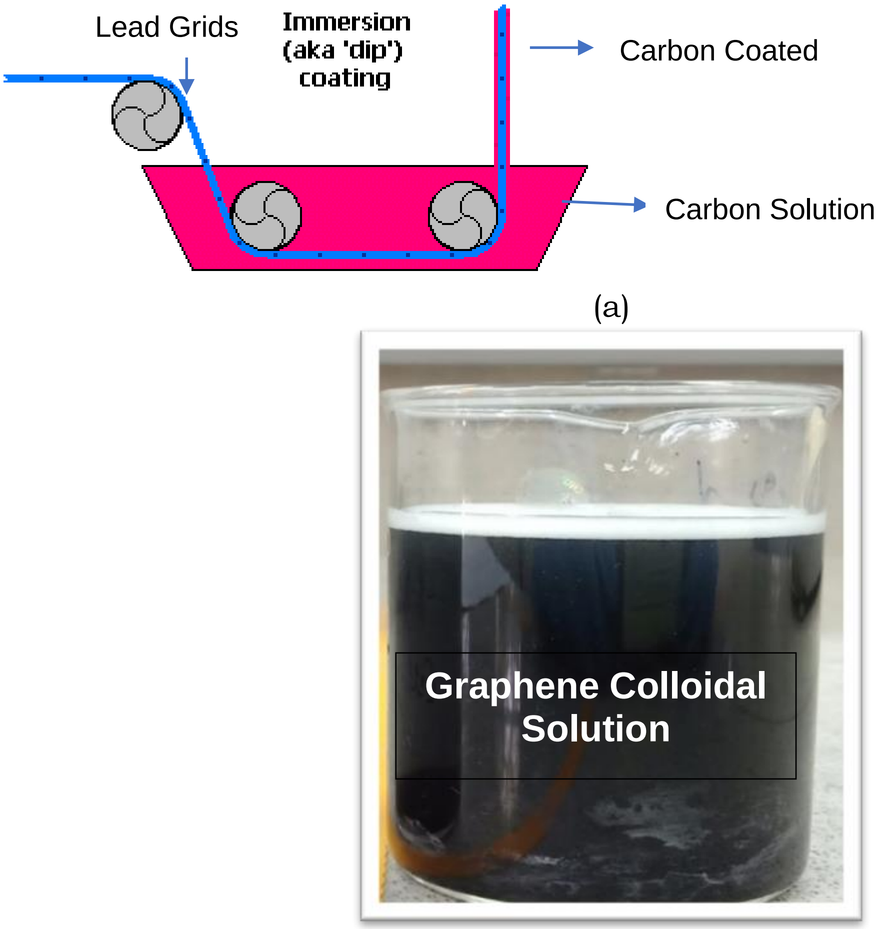
Chemical quantities may be used in preparing the graphene colloidal solution:

1. Demineralized (DM) Water – 1000ml
2. Graphene – 5gms
3. Sodium Cholate salt – 5gms
4. Emeraldine salt – 5gms

Procedure may be followed in preparing the colloidal solution:

1. Graphene material is sonicated with Sodium cholate and Emeraldine salt for 60mins at ambient temperature.

2. Later all the materials are ball milled at 500RPM for 30mins in a planetary mill.
3. Add all the milled particulates in 1000ml of Demineralized water and stir for 30mins to achieve colloidal solution.



(a)

(b)

Fig 6.4 Coating Process – (a) Dip coating/Immersion process (b) Graphene Solution.

Three step procedure has been has arrived and validated the coating effectiveness on the grids.

Step 1: Heat treatment of the grids @150°C for 30 Mins.

Step 2: Dip the grids in graphene Solution for 5Seconds.

Step 3: Drying the coated grids @105°C for 2Hours.

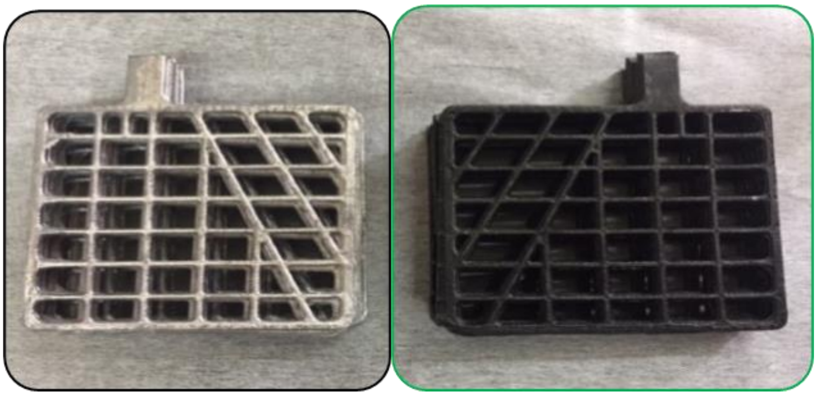


Fig. 6.5 Regular (Left) & coated grids (Right).

In detail Elemental analysis were carried out on coating importance and found out that the graphene participating

6.1.2 Active material pasting / Electrode preparation and Assembly

Along with the graphene, commercial-grade Binder, Blanc Fixe ($BaSO_4$) and Lignin is milled in a planetary ball mill at 500RPM for 15 Mins. This makes the material distribute and spread uniformly in the pasting process, The negative active material (PbO) was prepared at a temperature <65°C by mixing grey oxide with priorly prepared milled graphene materials, limiting the graphene to 0.2% of active material loading. This loading restriction has been based on the utilization of active material at formation. DM water was then added and made as a homogeneous mixture with a sulphuric acid solution of 1.40 specific gravity. The control batteries with commercial-grade carbon black of 0.2% are also prepared similarly, as mentioned above. After paste preparation, the lead alloy grids were machine-pasted with prepared pastes using a stainless-steel flat. The positive and negative electrodes were separated with AGM (Absorbed Glass Mat) separator, as shown in

Fig. 3. Later, the electrical characterizations of battery has been carried out by multiple steps programmed galvanostatic charging with the help of DTN-01 (Bitrode Instruments, USA) with built-in voltage and temperature measuring device as per Japanese Industrial Standard (JIS-5302:2004).

Initial Reactions:

PbO (Active Material) + H_2SO_4 = $PbSO_4$ + H_2O (1)

At curing the plate undergoes the following reaction:

(<70°C) $PbSO_4$ + 3PbO = 3PbO . $PbSO_4$ (3BS) (2)

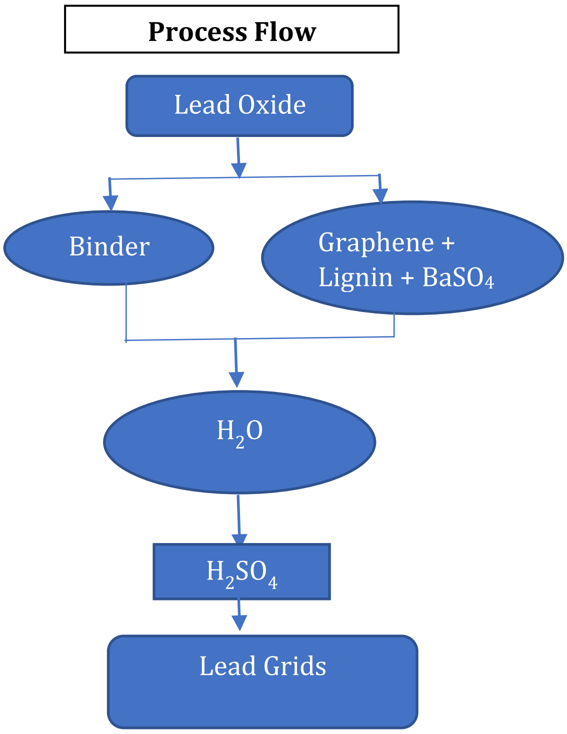


Fig 6.6 Flow chart of Negative active material preparation.

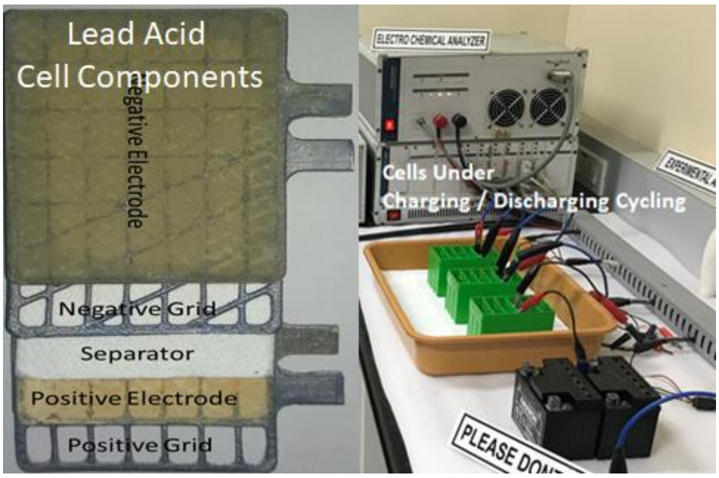


Fig. 6.7 Electrodes (+Ve & -Ve) & Test Assembly of the cell components

6.1.3 Acid Filling

Sulphuric acid is used as an electrolyte in lead acid batteries. H_2SO_4 provides electrical conductivity for the electrochemical reactions to take place. It acts as ionic conductor (Hydrogen and sulphates ions) and provides a medium for transfer of electrons as ions inside the cell. Compatibility of the electrolyte with active materials is an essential factor in choosing the electrolyte. For example, aqueous solutions cannot be used in lithium cells and organic liquids cannot be employed in lead acid devices. The specific gravity of the electrolyte is 1.29, the volume of it is about 9 to 10 ml per Ah for other manufacturers they do have 11 to 15 ml per Ah along with other additives like phosphoric acid, for effective recombination's. The acid filling process is a automated process where a filling tube is inserted to the individual cell holes of the battery as shown in the below fig. 6.8.

Fig. 6.8 Acid Filling process

6.1.4 Formation & Finishing

Cured plates are formed in dilute sulphuric acid that is electrochemically converted to the respective active materials namely lead dioxide in positive plates and spongy Lead in negative electrodes. This is carried out in a dilute solution of sulphuric acid usually of 1.29 or 1.3 specific gravity made for made from pure battery grade acid. The plates must be fully submerged in the acid before the formation is started, the plates of opposite polarity must be separated with a separator with each other having enough uniform space between them so as to avoid direct contact with each other so that the electrodes here absorb the electrolyte. The formation is carried out with constant current of 0.1 to 1.0 amps over a period of 24 to 36 hours depending upon the capacity of the designed battery. Below reactions takes place at the time of formation. Lawrence et al., describes the effects of different soaking times of the battery at the formation stages best compositions are affected by the time between the formation and the soaking of the batteries. However electrical results and examination of the former best suggest that soaking time is to affect the resulting battery performance as shown in fig. 6.9.

Formation: At individual electrochemical reactions,

(+Ve electrode) $PbSO_4 + 2H_2O = PbO_2 + H_2SO_4 + 2e^- + 2H^+$ (a)

(-Ve electrode) $PbSO_4 + 2e^- + 2H^+ = Pb + H_2SO_4$ (b)

Fig. 6.9 Formation by soaking the batteries in water <30°C

Below are the reactions happening in the batteries while performing in the field.

Discharging/Charging reactions:

-Ve electrode (Half Cycle):

$Pb + H_2SO_4 \leftrightarrow PbSO_4 + H^+ + 2e^-$ ($E^0 = 0.356$ eV) (1)

+Ve electrode (Half Cycle):

$PbO_2 + H_2SO_4 + 2H^+ + 2e^- \leftrightarrow PbSO_4 + 2H_2O$ ($E^0 = 1.685$ eV) (2)

Total voltage/potential across the electrodes: 0.356 + 1.685 = 2.041 eV

6.2 Process Validation

The process validation of the battery's will be carried out parallelly at the time of the component fabrications each step will be check it thoroughly and based on the specifications determine the quality of the components allowed for making the battery. In electrode (pasting process) preparation the battery electrodes are tested with the density of the active material and the vibration analysis of the plates. The active material, conversion of lead oxide powder to lead sulphates and also evaluating the free lead content in the active material is evaluated after the curing procedure.

In assembly, the main quality checks will be a round of the polarity check of the electrodes and then the intercell welding of the electrodes where all the electrodes are connected in series in the cells.

In acid filling, the lower limit and upper limit of the electrolyte is measured thoroughly before sending it for the formation if there is any low electrolyte feeling then the rest will be top-up, if there is an excess amount of electrolyte presence then those electrolytes will be dumped out of the design levels of the battery.

After formation, the electrodes are check for the conversion rate of the sulphates and lead oxide powder to lead dioxide in the positive plate and spongy lead in the negative plate. The best conversion rate will be considered for the manufacturing of the battery and also the High-Rate Discharge (HRD) test is carried out for the batteries to meet the requirement for dispatching the customers.

From our work to address premature failure, we validated the lead grids with and without coating process by the optical micrographs and elemental analysis by EDAX.

6.3 PMF: Optical Micrograph

In Fig. 10 an optical micrograph (Nikon Optima, Japan) reveals us the coating thickness with the black line on the surface of the lead grid with ~20 microns.

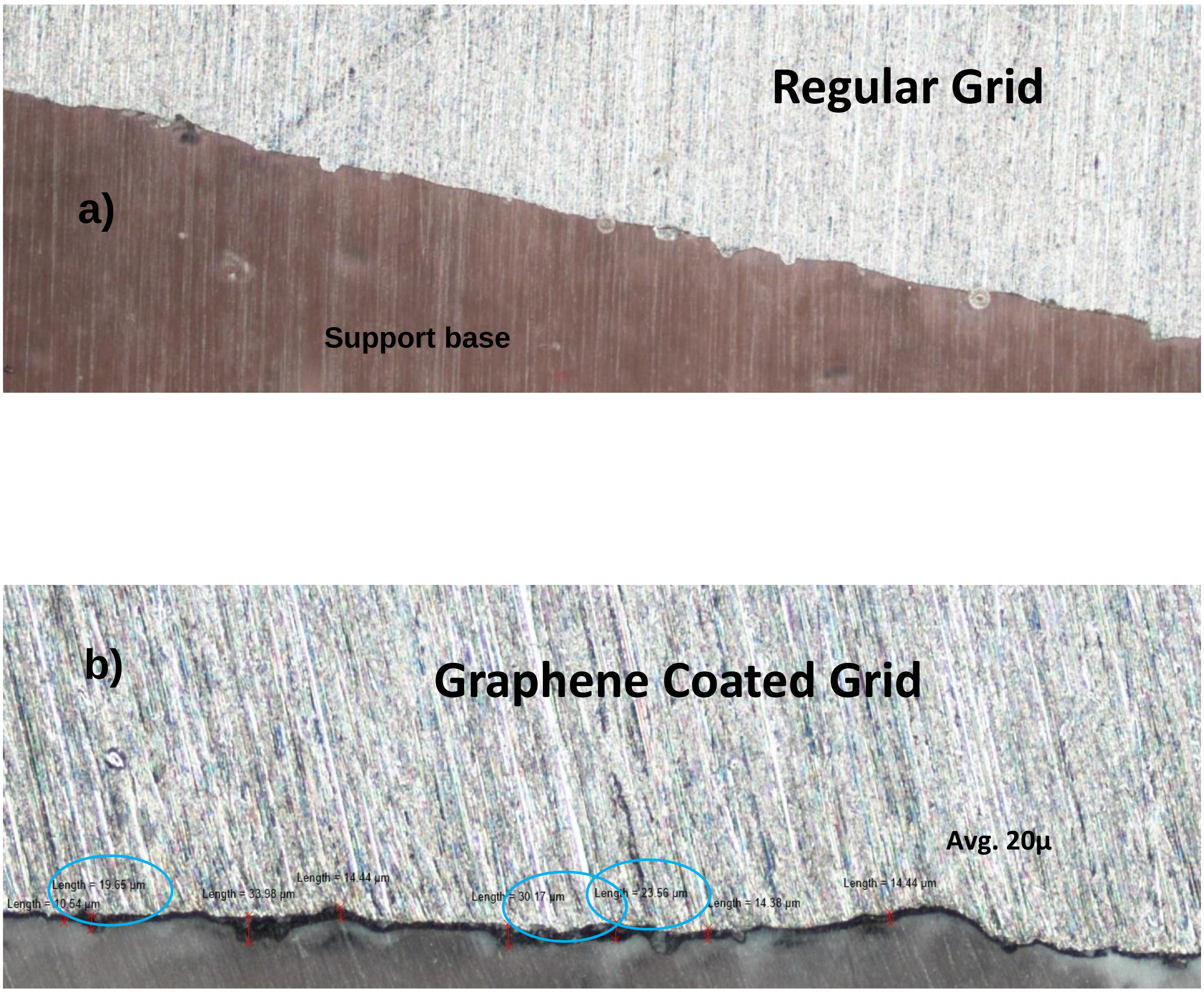


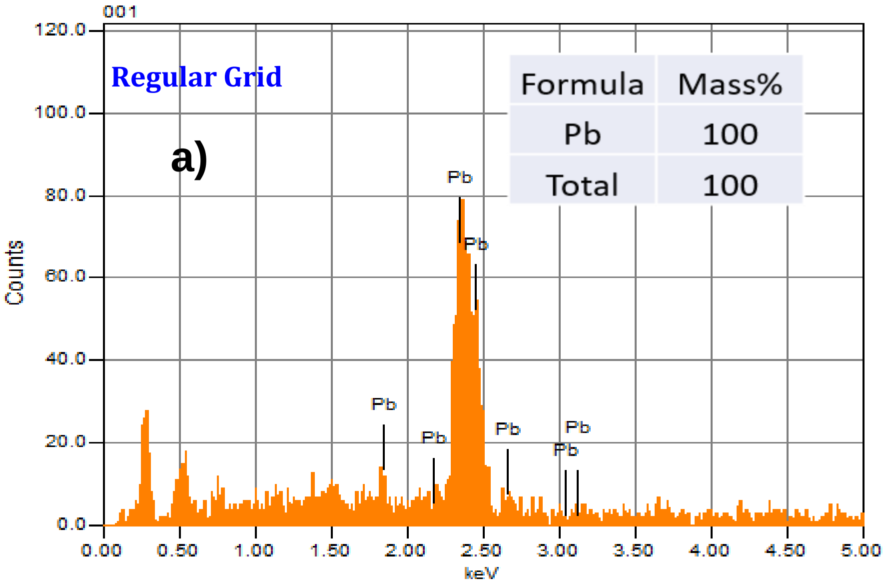
Fig. 6.10 Optical Micrographs of the lead grid surface.

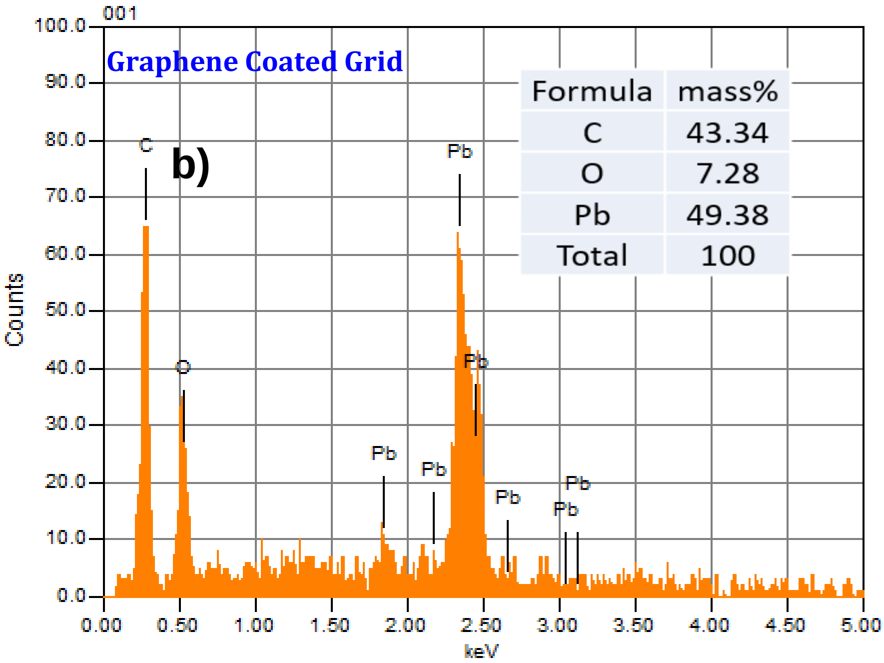
(a) Uncoated grid (b) Graphene coated grid with thickness ~ 20microns.

6.4 PMF: Energy Dispersive X-Ray Analysis (EDAX)

Elemental analysis of the uncoated and coated lead grids is captured (Fig. 6.11). Further the grids were pasted and cured as per the process. These cured plates are later verified for the formation of sulphates on the grids.

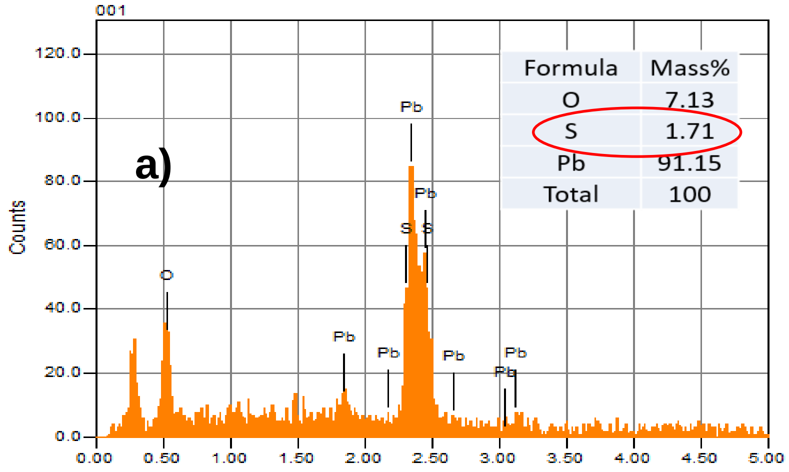
In prior art by M. Saravanan et. al., (2015) provided in Fig. 2.11, there the presence of sulphur after coating was observed, which creates the raise of resistance in the electrode. But, whereas with our approach it is evident that with the successful coating the grids have effectively restricted the formation of sulphur/sulphates on the grids (Fig. 6.11(b) & 6.12(b)) and expected a better battery performance.





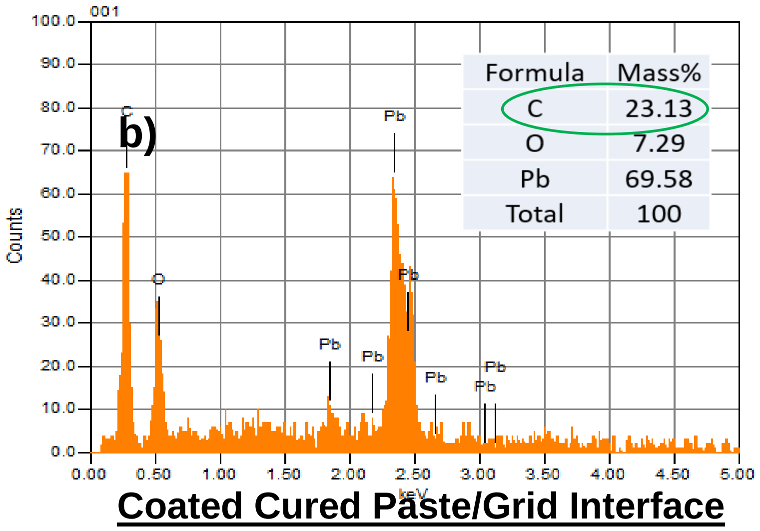
Formula	mass%
C	43.34
O	7.28
Pb	49.38
Total	100

Fig. 6.11 Elemental analysis of the grid (a) Regular / Uncoated Grid (b) Graphene coated grid.



Formula	Mass%
O	7.13
S	1.71
Pb	91.15
Total	100

Regular Cured Paste/Grid Interface



Formula	Mass%
C	23.13
O	7.29
Pb	69.58
Total	100

Coated Cured Paste/Grid Interface

Fig. 6.12 Elemental analysis of the cured electrode (a) Regular / Uncoated Grid (b) Graphene coated grid.

For addressing the progressive failure (PGF) we prepared batteries with graphene aided negative active material and the electrodes are evaluated by Cyclic voltammetry and Impedance analysis.

6.5 PGF: Cyclic Voltammetry

The prepared electrodes are subjected to cyclic voltammetry studies with the equipment supplied by Wonatech, Korea. The counter electrode used was a platinum electrode and the reference electrode was Standard Calomel Electrode (SCE). The sweep potentials were maintained from -1.0V to 2.5V with a scan rate of 50mV of the active area 1cm^2. For Lead Alloy analysis: Platinum was used as a counter electrode. For Electrode Plates: +Ve/-Ve plate of the lead acid cell was used as the counter electrode. Keeping calomel electrode as a reference electrode for all the electrochemical analysis. The initial rise of the current peak ~0.2A at -0.5V show in the Fig. 6.13 is the evidence that the prepared electrode is porous tend the electrolyte accessibility for reversible redox reaction, when compared to the control electrodes. It is also understood that the free lead present is converted to $PbSO_4$ by the addition graphene. Based on this the reactivity of the Graphene electrodes are better than the control one. The measured specific capacitance from the CV curve with the below equation (1) of the Graphene electrode is ~0.63 F/gm while carbon black-based control electrodes are of ~0.52F/gm, where a ~21% higher specific capacitance is observed with Gr electrode.

Calculating The Specific Capacitance by voltammetric study from below equation 1.

$$C = c/m \; (c=Q/V;\ Q=\int A/v) \qquad -\ (1)$$

c = capacitance

m = Mass (g)

Q = charge

A = Area

v = Scan rate

V = Potential Window

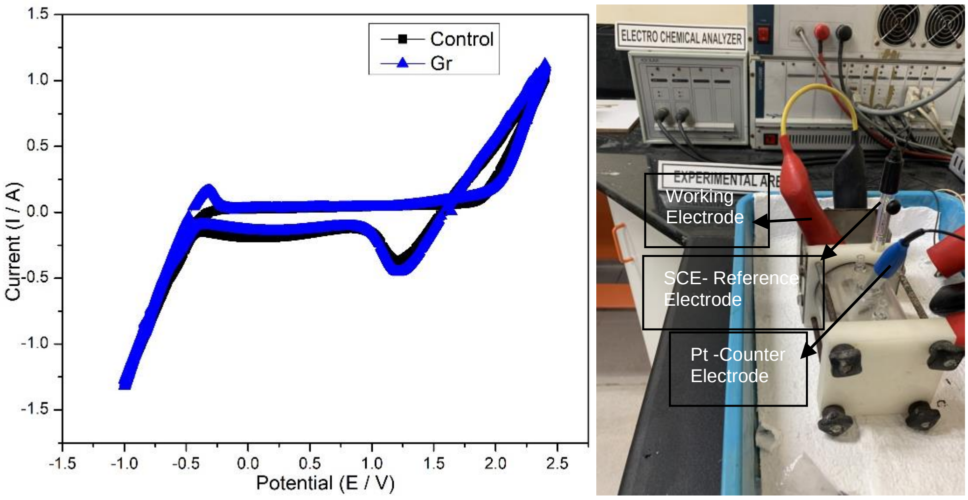


Fig 6.13 CV curves of Control and Graphene (Gr) electrode with experimental setup to the right

6.6 PGF: Impedance Spectroscopy

EIS are performed with the equipment Zive SP1, South Korea and Nyquist plots are developed by two electrode mode with graphene and without graphene. The EIS test was carried out with the amplitude of 10mV and the frequency ranging 1KHz to 0.1Hz. First, thing noticed from the plot that the graphene curves are much lower when compared to the control plot. This highlights the resistance of the gr electrode to be low to that of control. This means that the conductivity of the Gr electrode is high and dispersed uniformly. The illustration from the Fig. 6.14 gives us the parameters associated to the electrode behaviour. The electrode electrolyte interference resistance, Electrode charge transfer resistance and Warburg resistance and obtained and tabulated in Table 1. These results suggest that the addition of Graphene significantly reduces resistance developed from the reaction w.r.t to the electrolyte and electrode surface promoting the redox reaction more effectively. The Warburg Resistance is observed lower attributing to the porous structure, which promotes the ions diffusivity. Lower W leverage higher diffusivity between electrode and electrolyte interface.

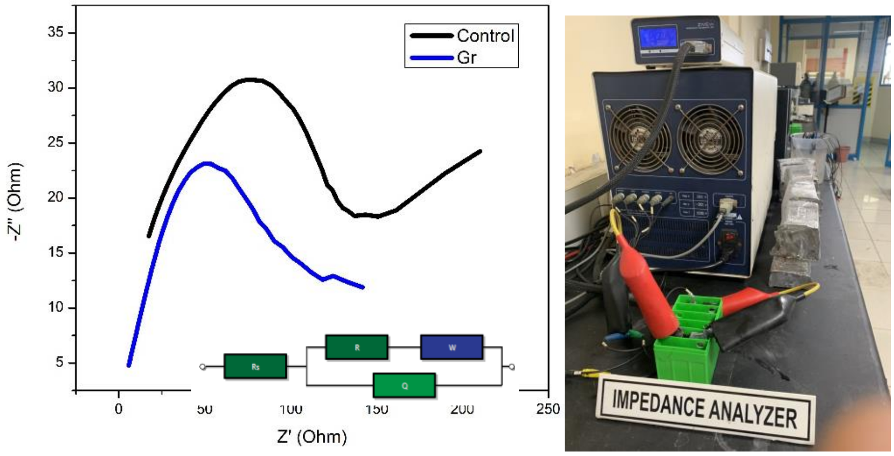


Fig 6.14 Nyquist Plot of control and graphene electrode with the experimental setup to the right (Inset: Equivalent Circuit).

Table 1. EIS parameters of control and graphene electrode.

Parameters	**Control**	**Graphene (Gr)**
R_s (Electrode/Electrolyte Resistance) Ω	11.64	2.97
R_{ct} (Charge Transfer Resistance) Ω	99.32	59.64
W (Warburg Resistance) Ω	0.04	0.01
Q (Capacitance) F	11.38	18.94

6.7 Summary

Electrodes with carbon coated grids are prepared and analysed before assembling into the device. Similarly, the electrodes with graphene aided negative active material were also prepared and evaluated before going for battery assembly. The analysis has confirmed the desired electrodes are in better position than the regular and can take for assembling the batteries. The coated batteries for stationary application are prepared and the batteries with graphene in negative active material were prepared for automotive application for further electrical assessment. With both approaches the batteries are made with AGM technology. The advantage of an AGM technology battery search that the batteries do not require water addition throughout their life & also user-friendly battery in the sense that evolves negligible number of gases in the normal course of operation and there is no acid seepage.

Chapter – 7
Results & Discussion

There are several standards to be complied when an energy storage device is made, to ensure the prepared device is ready to meet the specific requirements like discharge capacity, charge acceptance, cranking ability and life cycling w.r.t application. These standards include International Electrotechnical Commission Standard (IEC); the British Standard (BS/EN); Deutsches Institut für Normung Standard (DIN); The Japanese Industrial Standard (JIS); Telecommunication Engineering Commission (TEC), and so forth. As IEC/TEC & JIS are widely known standards for the stationary and Automotive applications and hence were followed for our studies.

7.1 Application of Graphene to improve Lead Acid Battery Performance

For Stationary Application (PMF):

The validations of high current discharges include 10, 8, 5, 1 hour, 15 Minutes and 5 Minutes tests on the 2V lead acid cells with graphene coated and uncoated lead grids have been conducted.

For Automotive Application (PGF):

1) Capacity/Energy density: The capacity of automotive batteries is rated at 10 hours, which means that the battery should last for the stated duration when discharged at a given current. For instance, a battery with a capacity of 3 Ah should last for 10 hours as it discharges at a current of 0.3A.

2) High Rate Discharge (HRD) Test: To evaluate the cranking ability of the battery at cold condition (-15°C).

3) Charge Acceptance Test (CAT): To estimate the time taken for recharging the battery.

The rating tests were carried out at Amararaja Batteries Limited, Tirupathi, India. Table 7.1 shows the characteristics of battery samples being prepared with positive coated grids.

7.1.1 PMF: Electrical Performance of positive Coated grids (2V-660Ah)

The capacity test of the cells with high current discharge were carried out. The C10, C8 and C5 hr test showed that the cells with coat and uncoated produced more than ~100% capacity with ease. But at C1 hr test the regular cells were found to be struggling and produced marginal higher to 100% capacity. Whereas graphene coated grids have comfortably delivered ~115%. When comes to C15 mins the regular cells were able to deliver only ~75% capacity and the coated batteries were able to deliver ~154% capacity, which is significant superior. And when test for C5 mins capability the regular grids were just limited to ~56% and the graphene coated cells continued to deliver ~156% capacity. Overall, the cells with graphene coat on the positive grids have performed better than the regular uncoated grids as presented in below graph Fig. 7.1. This significant improvement could be very much useful for peak load requirement at on/off grid stationary application.

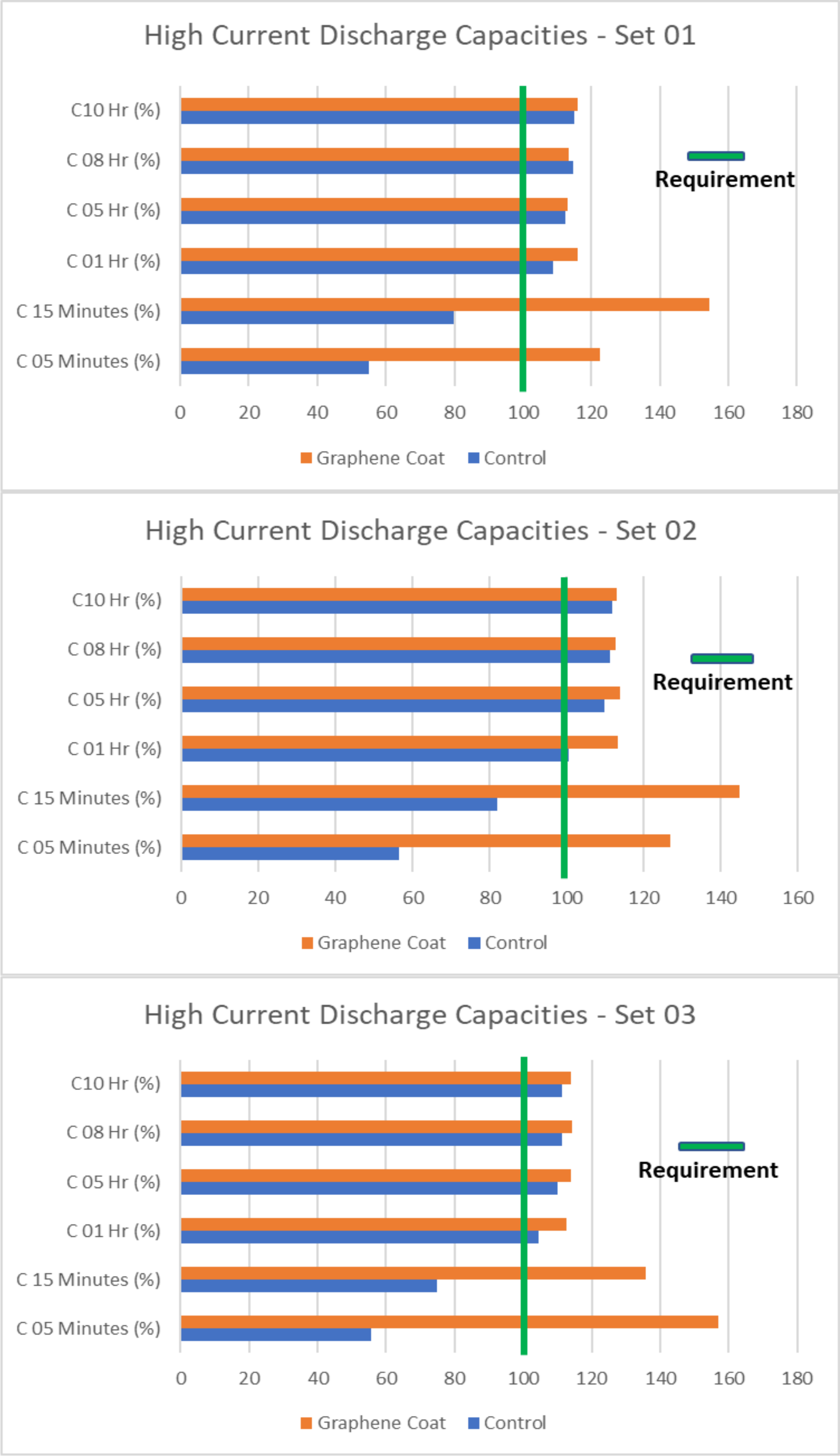


Fig. 7.1 Electrical assessments of coated and uncoated lead grids with 03 times repetition.

7.1.2 PGF: Electrical Performance of Graphene in NAM (12V-3Ah)

(a) Discharge Capacity:

The performance of the battery was tested for its discharge capacity in the range of Cn/10hr. The current test rating is expressed in terms of the nominal capacity of the battery, calculated at 95% utilization of the active material. Fig. 7.3 shows the comparison between the discharge capacity of batteries comprising reduced graphene oxide with that of control batteries. All the tests were conducted at 25±20C. These batteries were discharged with 0.1C rate to a cut-off voltage of 10.5V. It is observed that the discharge time of test batteries with graphene oxide is longer compared to that of the control batteries. Further, it is observed that the current discharge capacity increased by nearly 27% when Graphene is added to NAM in comparison to control batteries. These improvements are attributed to the conversion of the active material to a large extent.

Test Conditions:

Environment: 25°C ± 2°C; Discharge with I10 Current; Cutoff voltage 10.5V;

Duration t(h) recorded C10 (Ah) = I10 * t

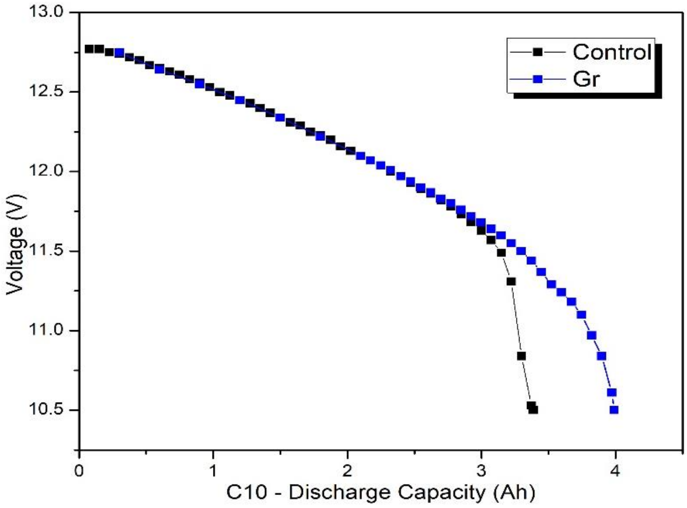


Figure 7.3: Discharge Capacity of Control vs Graphene battery.

Observations:

1. Uniform conductive network,
2. Higher active material utilization, due to small & porous structure.
3. Maintains the thirst for active mass towards acid.
4. Improved discharge capacity (~27%).

(b) Charge Acceptance (CAT):

Charge acceptance is one of the important performance characteristics for batteries in applications involving high depth of discharge (DoD). A higher charge acceptance capacity of a battery extends battery cycling life. The charge acceptance is measured at the 10th minute by applying a constant voltage of 14.4V. The observations from fig 7.4., confirms an enhancement of 14% in charge acceptance is observed when compared to control batteries by adding Graphene to NAM. Initially, the lower current intake was observed with the Graphene battery, this is due to the resistance buildup in the electrodes. With the intake of the current, the sulfates causing the resistance is reduced over the period and later increase the current intake. This is due to the availability of adequate Graphene with a unique flexible porous structure that promotes better transport of hydrogen and sulfate ions. Further, it promotes improved utilization of active mass and uniform distribution of sulfates.

Test Conditions:

Environment: 25°C ± 2°C; Discharge with I10 Current, for 5hrs; Store at 0°C ± 2°C for 6hrs; Charge with 14.4V ± 0.1V @ 10min Duration is recorded.

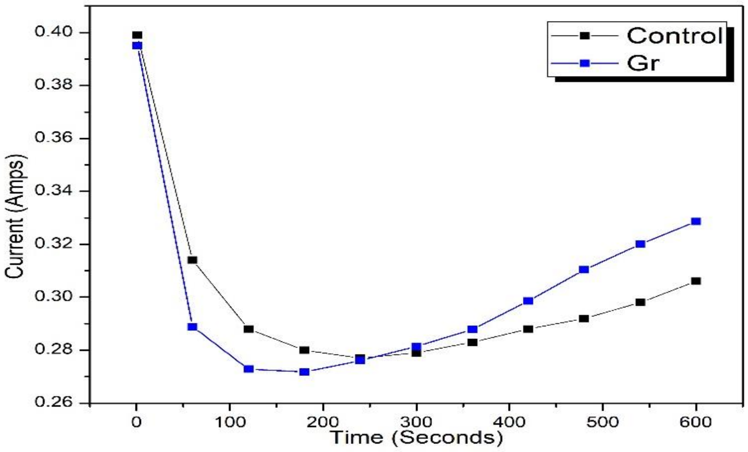


Figure 7.4: Charge Acceptance of Control vs Graphene battery

Observation:

Unique porous structure,

Facilitates H+ & SO4- ions,

Uniform distribution of sulphates &

Improves active material utilization.

Improved charge acceptance (~10%).

(c) Cranking Ability (HRD):

High-rate current discharge attributes to the cranking ability when a battery is discharged at comparatively high current as per the storage capacity of battery. HRD feature is carried out as per the conditions, to measure the voltage, after the start of discharge and till the completion time. Generally, the batteries meet the 5th-sec voltage requirement as per JIS standard; hence, we have not mentioned. But the time taken to reach 6V, while discharging @ -15°C fumbles, this has been addressed in the following.

Battery (12V/3Ah) life gets affected when the discharge current exceeds the rated discharge current during the vehicle start-up. Hence the study on high-current (30A) discharge assumes importance in characterizing battery performance. It is observed from fig 7.5. That the time taken for the discharge capacity of the batteries with Graphene exceeds the requirement and for a long-time-interval of 23% (23s). This represents the performance improvement over control batteries in terms of high-rate current discharge.

Test Conditions:

Environment: -15°C ± 2°C for 16hrs; Discharge with 30A; Cutoff voltage 6V; Duration t(min) recorded.

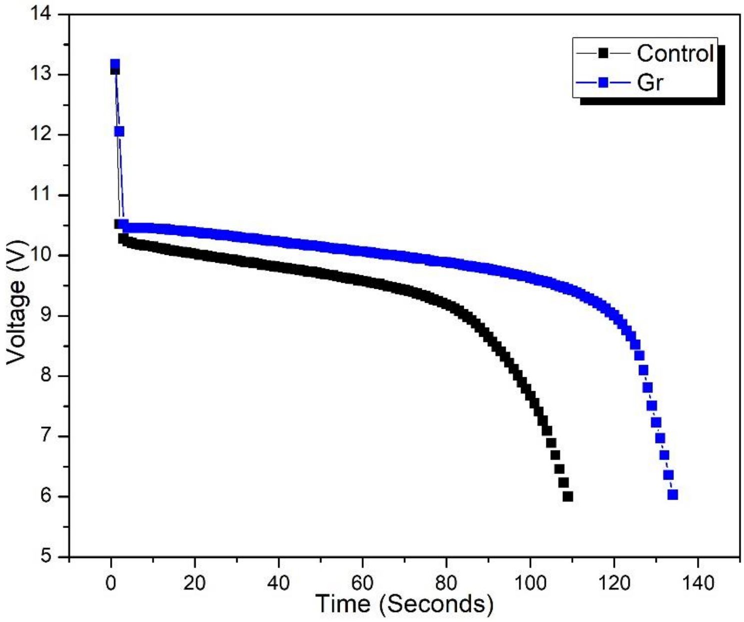


Figure 7.5: Cold Cranking ability of Control vs Graphene battery

Observation:

At HRD, discharge current exceeds rated discharge, which impacts capacity. Reaction happens only on the surface of the electrode, which lead to large sulfates formation, hindering the conductivity. Improved cranking ability (~23%).

(d) Life Cycle Performance:

The cycle life of a battery (12V/3Ah) is defined as the complete number charging (0.6A) and complete discharging (3A) cycles, before its capacity drops to ~30% of the original capacity. This test is concerned with the frequency (number of times) at a repetition of charging and discharging of high load area with discharge depth of 100% of each cycle and limiting to 30% State of Health (SoH) cut-off condition, making this as one of the critical battery performance indicators.

Test Conditions:

Environment: 40°C ± 2°C; Discharge: Current 3A, for 1hr, Cutoff voltage 10.2V; Charge: Current 0.6A, for 5hrs, Repeat for 25 cycles then Run Capacity Test @40%DoD, after every 25 cycles; Duration is recorded.

Run the test until <50% SoH of 80% rated capacity.

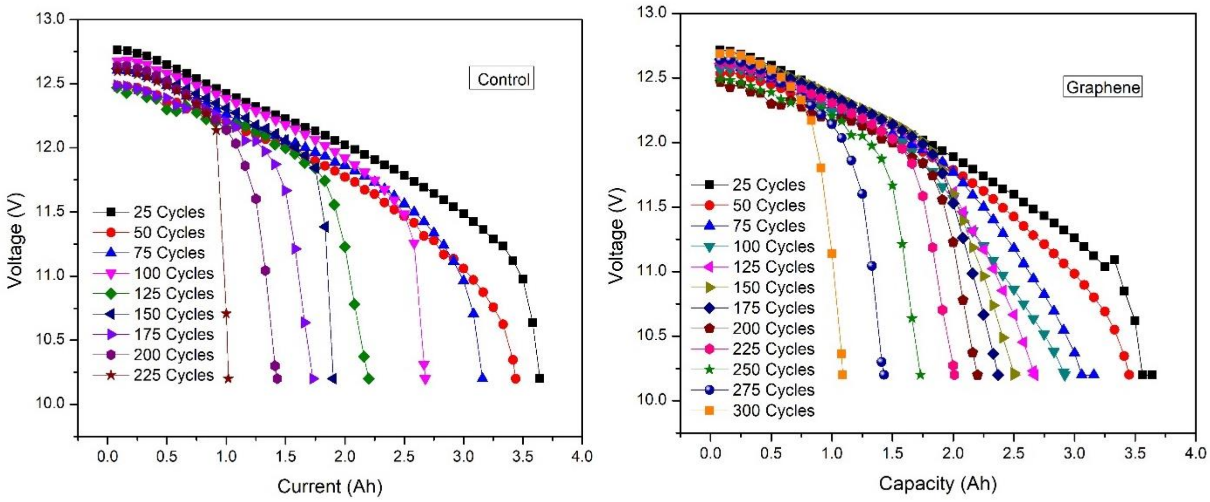


Figure 7.6: Life cycling ability Control battery (Left) and Graphene Battery (right)

Fig. 7.6 shows the cycling behavior of Gr batteries at a 1C discharge rate. It is observed that at 225 cycles, the control batteries show a drop in the discharge capacity and failed to recover. Whereas the cells with Graphene layers in the negative active material performed up to 300 Cycles with a stable discharge. This may be attributed to lowering the internal resistance of the cells due to limiting the formation of larger sulfate crystals. From this investigation, it is observed that by adding, Gr in NAM increased charge acceptance as well as restricted the sulfation in the negative electrodes during the deep discharge cycling of the batteries. The charge /discharge cycling of the batteries, with Graphene layers, have a ~33% enhancement when compared to that of the control batteries. From Fig. 7.7, SEM images of the negative electrode with Gr have relatively small $PbSO_4$ when compared with Control electrodes. We can conclude that with the addition of Gr in NAM, we can increase the active material utilization with enhanced discharge capacity and higher life cycles. Higher life of the battery gives us an additional benefit of cost for replacing the battery after its end of life. Adding an advantage to the environment towards recycling.

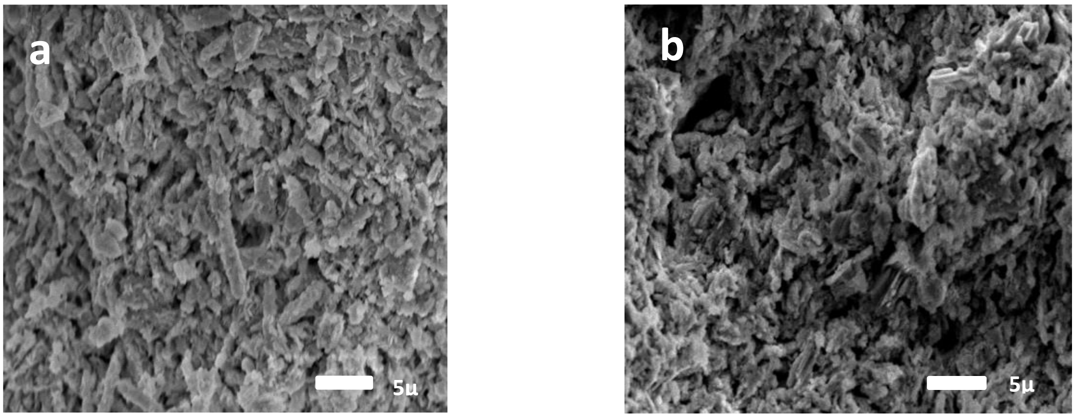


Fig 7.7. SEM Images after end cycles a) Control b) Gr

7.2 Summary

In the present investigation, graphene is prepared using exfoliated graphite through the microwave irradiation technique. Performance studies are conducted on Lead Acid Battery to determine the effect of graphene as a coating material for stationary application to successfully restrict the premature failure (PMF). Othe area, the progressive failure (PGF) has been addressed by using graphene as an additive in Negative Active Material (NAM) for automotive (2Wheeler) application. The performance test results are compared with the performance of control batteries. The effects of the addition of this graphene material on battery performance like discharge capacity, charge acceptance, cranking ability & cycling performance were investigated and found better.

Premature Failure (PMF):

The 2V-600Ah lead acid cells developed with graphene coated grids have enhanced the high current discharge at short durations of C15 Mins – 2x times and

C5 Mins – 3x times when compared to the control cells. This significant improvement was achieved by limiting the growth of the sulfate on the girds and providing a conductive network at high current discharges.

Progressive Failure (PGF):

When graphene is used as an additive in the negative active material and developed a 12V-3Ah batteries, the discharge capacity has enhanced (~27%) to a large extent with a cranking ability higher of ~23%. In addition to this, the batteries with the graphene exhibit ~33% higher stable life cycle performance. This significant improvement was observed by limiting the irreversible sulfation of the negative electrode, improving its charge acceptance ability (~14%) by providing a conductive network during charge and discharge cycles.

The emphasis on graphene as an additive material for lead acid batteries is our first attempt, and this could lay a platform to develop advanced lead-acid batteries for high-rate partial state of charge applications like HEV/EV’s.

CHAPTER – 8

CONCLUSIONS

In this chapter, salient features of our work have been highlighted, and an attempt to summarize our research has been made. In addition to this, a broad vision for future research work has also been provided.

8.1 Summary of the present work

This chapter presents the overall conclusions from experimental investigations conducted on Absorbed Glass Mat Lead Acid Energy Storages are presented. In this work, our scope is to improve the electrical performance of the lead-acid energy storages with graphene material by addressing two critical failures happening in the battery (1) Premature Failure and (2) Progressive Failure for stationary and automotive applications respectively.

In the present investigation, graphene material is studied to address the premature and progressive failure of energy storage. In this thesis, preparation of Graphene material, characterization and analysis of graphene-based electrodes subjected to the electrical characteristics were carried out. In the investigation process, two approaches are investigated (1) Colloidal form of graphene for premature failure & (2) Powder form of Graphene for Progressive failure of the energy storages.

Taking forward with Electrodes: Preparation, characterization, assembly and electrical performances has been done and the results are presented. The electrical performances like Initial Capacity (Energy Density), Charge Acceptance (Recharging behavior), Cold Cranking (High current discharges), and Life cycling test were performed on the graphene-based devices and have been compared with the devices without graphene material. The essential conclusions drawn from this present work are as follows.

The preparation of materials was crucial since it can affect the electrode characteristics considerably. The study concluded that the 2-dimensional material is found that its contribution towards the electrode's performance has enhanced significantly in a cost-effective way.

Various methods for synthesizing graphene were analyzed and optimized for a novel approach to synthesizing graphene in bulk with cost-effectiveness. Using the aqua regime, graphite was partially oxidized and then exposed to microwave radiation to get graphene worms. By sonicating these worms in the solvent environment until a uniform solution is achieved, followed by solvent evaporation to collect our desired 2d material.

In conclusion, initially using the Hummers method Graphite Oxide (GO) was prepared. Further exposure of GO to microwave irradiation followed by ultrasonication we obtained with Few Layered Graphene (FLG). The synthesized material's cross-sectional morphology, structure, and phase studies were carried out using many characterization tools like Surface area analyzer, scanning electron microscopy (SEM), x-ray diffraction, transmission electron microscopy, and Raman spectroscopy. Resistance values of the prepared material were calculated with an in-house developed test rig setup.

Due to its outstanding physical and chemical properties, graphene plays a good role as an electrode material and makes it possible to produce high-performance energy storage devices (Lead Acid).

The essential conclusions drawn from the present work are as follows:

(a) Premature Failure (PMF)

Positive grid corrosion is the phenomenon revealed that the cause of the failure is the formation of a barrier layer of lead sulfate growth between the grid and the active material. To restrict the formation of the passivation layer, we have coated the grids with a graphene-based solution and found that the coated grids are more corrosive resistant than the uncoated grid. The grid growth studies were extensively carried out.

(b) Progressive Failure (PGF)

The optimal composition of graphene with an active material to achieve the device's maximum efficiency was critical. Several compositions were analyzed in terms of Elemental concentration, conductivity, and pH. After identifying the optimal composition and preparing the electrodes, quality checks were carried out. After analyzing the electrodes in terms of active material conversions, these electrodes were further studied with Cyclic voltammetry and Electrochemical impedance spectroscopy. After the evaluation, the electrodes were assembled connected in series to form a 12V battery for further electrical evaluation.

Keywords: Carbon; Nanomaterial; Graphene; Lead Acid Battery; Lead Grids; Negative Active Material; Premature Failure (PMF); Progressive Failure (PGF); Sulphation; Stationary Lead Acid Battery; Automotive Lead Acid Battery; Japanese Industrial Standard (JIS); High Current discharges; Energy density (Capacity); Charge Acceptance; Cranking Ability; Charge/Discharge Cycles.

The outcomes of this experimental investigations from the synthesis of different nanomaterials to applications are listed below. And found in the below link.

https://scholar.google.co.in/citations?hl=en&user=OD8c83cAAAAJ&view_op=list_works&sortby=pubdate

Publications:

1. Effect of Milled Carbon as Negative Electrode Additive for Lead Acid Energy Storage Device – 2020.
2. Synthesis and study of reduced graphene oxide layers under microwave irradiation – 2018.
3. Facile synthesis and thermal analysis of antimony telluride nanostructures – 2018.
4. Synthesis of dendritic-flowers of wurtzite Cu_2ZnSnS_4 via solvothermal process – 2017.
5. Synthesis of Graphene Oxide by Modified Hummers Method and Hydrothermal Synthesis of Graphene-NiO Nano Composite for Supercapacitor Application – 2016.
6. Synthesis and analysis of ternary oxide nanomaterial for electro-thermal applications - 2015.
7. Synthesis and evaluation of zinc-based nanomaterials for optical-thermal studies – 2015.

8.2 Scope for future work

With the success of this work in identifying potential areas of improving the electrochemical behavior attributed to the grid (Current collector) surface and with unique morphology of low dimensional material used along with the lead oxide as a precursor for lead-acid batteries has revealed the future opportunities and efforts to fulfill the global objective and needs in producing a prototype of lead-acid hybrid supercapacitor battery.

Based on the results from this work, future research will emphasize the following:

- The carbon-coated lead grids with different coating thickness for HEV & EV applications.
- The mesoporous carbon materials are to be extended into the making of producing electrodes to meet objective cost and scalable production feasibility.
- Identifying a common reducing material of the sulfation formed on electrode surface due to the interaction with the electrolyte.
- Constructing a prototype of lead-acid hybrid battery with supercapacitor behavior with the carbon materials in both positive & negative electrodes for evaluation.
- Develop a battery with No lead grids by replacing with Carbon electrode.

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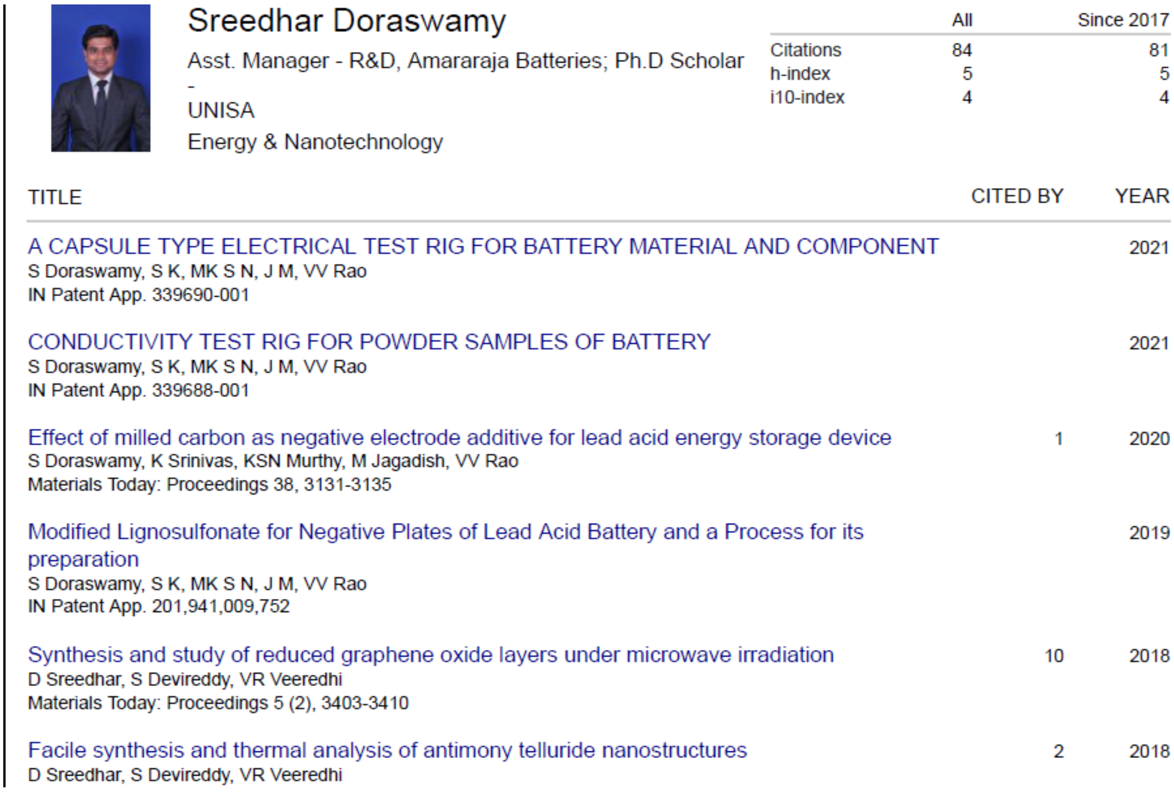

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Fabrication and Mechanical Properties of AlSi12 Nano Particulate Composite S Reddy K, S D, N P, J Raju G Procedia Materials Science 10, 149-158	4	2015

Annexure - A

1. Comparison of Materials for Lead Acid Battery application

Why Carbon?

S. No	Properties	Carbon	Silver	Copper	Gold	Tungsten	Nickel	Platinum	Tin	Titanium
1	Structure	Hexagonal APF: 0.74; Porous/Non Porous	Face Centered Cubic ; APF: 0.74			BCC; APF: 0.68	FCC; APF: 0.74	FCC; APF: 0.74	BCT; APF: 0.687	Hexagonal APF: 0.74
2	Density (g/cm3)	1.8 - 2.1	10.49	8.96	19.3	19.3	8.9	21.45	7.2	4.5
3	Surface Area (m^2/g)	10-1400	1.8	0.02	4	0.18	0.7	22	12	32
4	Conductivity (10^6 S/m)	10-100	63	59.6	41	17.9	14.3	9.43	9.17	2.38
5	Inertness (H_2SO_4)	Unreactive	Reactive		Unreactive		Reactive	Unreactive	Reactive	
6	Melting Point (°C)	3550	961	1084	1064	3422	1455	1768	231	1668

Ref:

1. doi: 10.1149/2.062301jes
2. doi: 10.1016/j.jpowsour.2017.01.056
3. ISBN: 9783642582622
4. Patent No: EP0435766A2
5. ISBN: 9781118686232

2. Carbon Exploration as Lead acid battery additive Materials

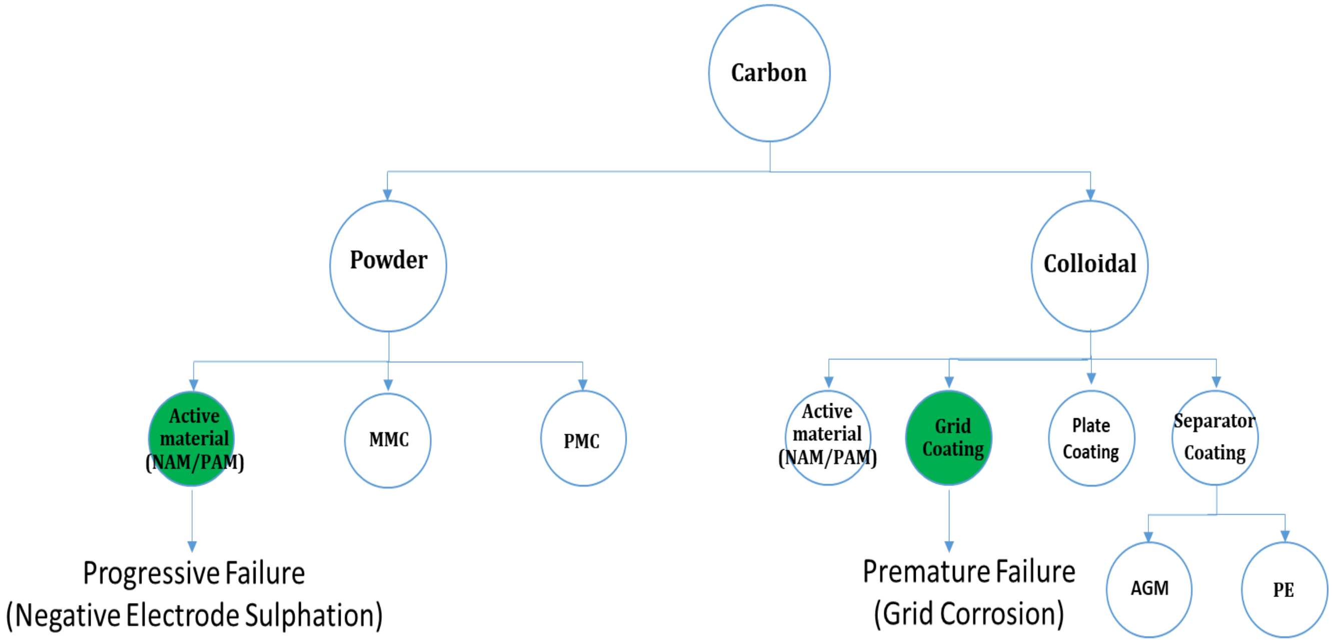


Fig. Classification in terms of usage.

3. Role of Nanocarbon materials in Lead-Acid Battery: Application and Requirements

Nanocarbon (NC) in different formulations play a vital role in different applications. The following table explains various applications and intended benefit from NC.

Applications	Requirements	Nanocarbon Advantage
Advanced SLI (Start Light Ignition)	1) 90 % - 100% SOC 2) High Discharge current/Low charge current operation	1) Increase in CCA (Cold Cranking Ability) 2) Increase in cold charge current acceptance 3) Improvement in deep discharge recovery due to dark current in modern vehicles 4) Increase in life under deficit charge condition
EFB (Enhanced Flooded Batteries)	1) 75% - 100% SOC 2) High Discharge current/high Charge current operation	1) Increase in CCA 2) Increase in cold charge current acceptance 3) Improvement in deep discharge recovery due to dark current 4) Increase in SBA life cycle by 30% 5) Increase in 17.5% DOD life cycle by 30% 6) Maintaining higher dynamic charge current throughout the life 7) Increase in charge current acceptance at high SOC – 90%
AGM – LAB	1) 50% - 90% SOC 2) Low to Moderate discharge current/ Low charge current operation	1) Increase in life 2) Maintaining charging time throughout the life 3) Maintaining dynamic charge acceptance behavior throughout the life 4) Less to assimilate 102 to 105% previous discharge input
Tubular - solar	1) 20% - 100% SOC 2) Low Discharge current/ Low charge current	1) Increase in life 2) Maintaining charging time throughout the life 3) Maintaining dynamic charge acceptance behavior throughout the life 4) Less time assimilate 102% to 105% previous discharge input

Annexure – B

List of Instruments Used in this project:

S. No	Equipment	Make	Country	Application
1	SEM/EDS	Jeol	Japan	Elemental Composition,, Morphological Analysis, Topographical Analysis
2	XRD	Rigaku	Japan	Phase Composition, Crystal 3-D View, Crystalline Structure View, Sample Size Distribution View
3	ICP-OES	Agilent	Malaysia	Elemental Analysis Capable To Ppb Level
4	UTM-Universal Testing Machine	Tinius Olsen	U.K	Tensile/Elongation Test, Puncture Resistance Test, Pell Off Test, Flexural Modulus Test
5	Vickers Hardness Tester	Buhler	Germany	Hardness Measurement, Aging Studies
6	Stereomicroscope	Seiwa Optical	Japan	Microstructural Analysis, Alloy Characterization
7	Optical Microscope	Nikon	Japan	Macro And Micro Grain Structural Analysis Of Alloys
8	LOI	Fire Testing Technologies	U.K	Limiting Oxygen Index For Flame Retardant Poly Materials

9	DSC- Differential Scanning Calorimetry	Netzsch	Germany	Melting And Crystallization, Glass Transition Temperature , Polymer Materials Identification, Degree Of Crystallinity
10	BET-Surface Area Analyzer	Coulter Corporation	Usa	Surface Area Of Powder Samples, Porosity Measurements
11	Impedance Analyzer	Wonatech (Zive Sp1)	South Korea	Alloy Characterization, Impedance Measurements.
12	Electro-Chemical Workstation	Wonatech	South Korea	Potentiostat, Galvanostat, Corrosion Studies, Electro Chemical Behaviors.
13	Ball Mill	Fritsch	Germany	Size Reduction , Uniform Mixing
14	Thermo Gravimetric Analyzer	Netzsch	Germany	Thermal Behavior Of Solids, Liquids, Semi Solid Materials
15	IZOD	Zwick	Germany	Impact Strength Analysis Of Polymers , Alloys, Metals
16	Wet Laboratory	Alloy Analysis, Separator Analysis, Effluent Water Analysis, Other Battery Components Analysis		
17	Electrical Resistance	Wonatech / Zive Sp1	South Korea	Test Rigs Inhouse Development And Power Source Connected To Wonatech

Annexure – C

Other outcomes through this project:

S. No.	Title	Status	Remarks
1	To developed the Electrical Test Rigs for Powder & Sheet Materials	Successfully designed, fabricated and commissioned the fixtures.	Commissioned and have been using for all types of conductive / Resistive type powder or sheet form materials.
2	MWCNT's as NAM Additive in Flooded LAB	Tests successfully carried out with 12V-65Ah rated flooded battery.	Paper Communicated to DHET Listed Journal of 'Current Applied Science & Technology (CAST)'.
3	Functionalized Silica as PAM additive in LAB	Tested for 12V-3Ah rated Battery	Performance better with gravity cast grid technology were encouraging and tests are under progress with stamped grid technology.
4	Carbon as current collector grid for LAB	Prototype developed with 2V-3Ah cell by replacing with developed carbon grid.	Successfully replaced the negative lead grid with carbon grid and observed slightly better results when compared to the control cells. Currently, under progress of replacing the positive lead grid with carbon grid.
5	Electrical Performance of Graphene	Prototype developed with 2V-3Ah rated	Tests were carried out with assembling by 3 iterations with the coated negative, positive and both the electrodes. It was observed that with the

	Coated Electrodes	batteries by coating electrode surface with developed colloidal Graphene solution	coating of negative electrodes leveraged in higher initial discharge capacity with improved HRD.
6	Electrical Performance of Graphene Coated AGM Separator	Prototype developed with 2V-3Ah rated cells by coating AGM separator with developed colloidal graphene solution	Tests were carried out with assembling by 3 iterations with the coated AGM facing the negative, positive and both the electrodes. From the electrical tests, no significant improvement in charge acceptance and cold cranking ability. The PSoC studies have improved with ~20% with both side coated separator facing the surface of positive and negative electrodes.
7	Electrical Performance of Carbon paper as plate backing paper	Tests were successfully carried out with 12V-38Ah rated flooded battery.	Carbon coated paper was less effective when the coted side is faced towards the electrode. But shown better adhesion when the coated side was faced outward to the electrodes. Later, electrical tests were carried out on the batteries which showed no significant improvement in the quick charge and discharge ability. But, found higher life in light load (~10%) and High Load (~20%).
8	Nanocarbon Particles as	Tests were successfully	Generally, carbon materials are explored in NAM only. But here we attempted to add nanocarbon

	PAM additive in LAB	carried out with 12V-38Ah rated flooded battery.	materials in liquid form which are available in the market. Electrical tests were carried out on these batteries which showed no significant improvement in the Charge acceptance and cold cranking ability. But, found higher life improvement in light load (~2 times) which is a significant indication to develop for high load studies for Hybrid/EV applications.

1. Electrical Analysis of Graphene Coated Electrodes

Graphene Coated Electrode

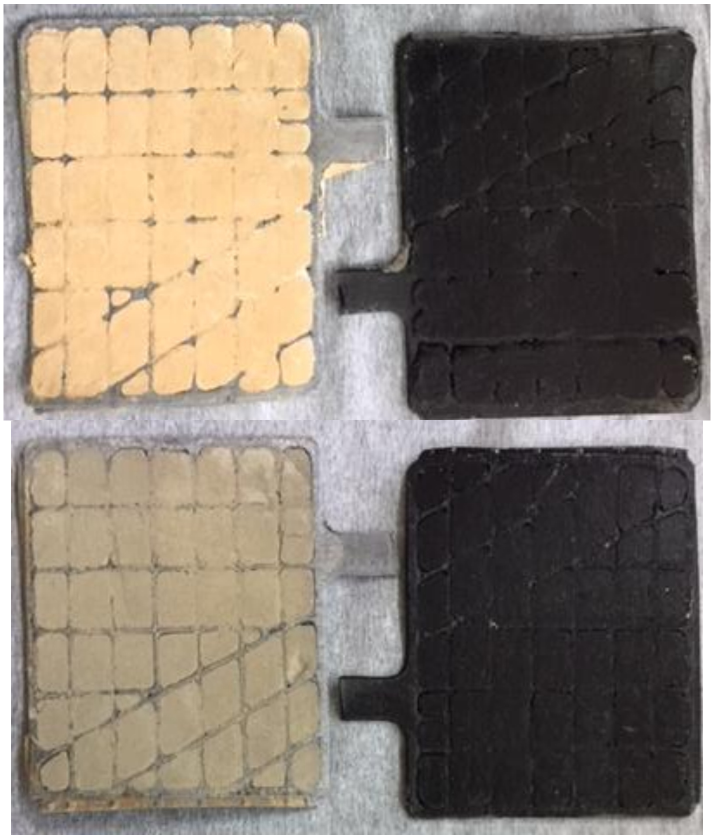


Fig. Electrodes with and without Graphene Coat.

Table. Electrical performance of Electrodes (with and without Graphene Coat).

S. No	Test	Requirement	Regular	-Ve Coat	+Ve Coat	+Ve & -Ve Coat
1	C10	95% Output	3.33 (Ah); 111.16%	3.54 (Ah); 118.0%	3.24 (Ah); 108.0%	3.44 (Ah); 114.66%
2	HRD	@ 5Sec (10V)	10.48V	10.23V	9.89V	10.06V
		108s (6V)	106s	160s	132s	125s
3	CAT	0.3A	0.32A	0.36A	0.32A	0.33A

Inference:
Successfully coated the plates with graphene and tested the batteries (12V-3Ah). Found that the Negative coated plates performed better when compared to the rest in terms of HRD time to reach 6V. And marginal improvement (~4%) in capacity.

2. Electrical Analysis of Graphene Coated Separator

Graphene Coated Separator

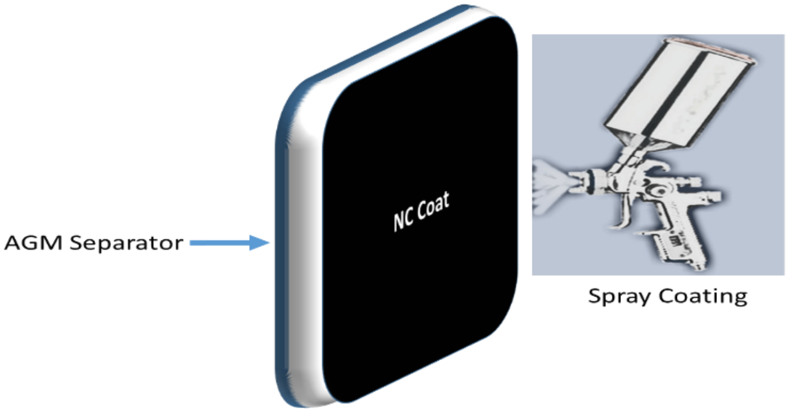
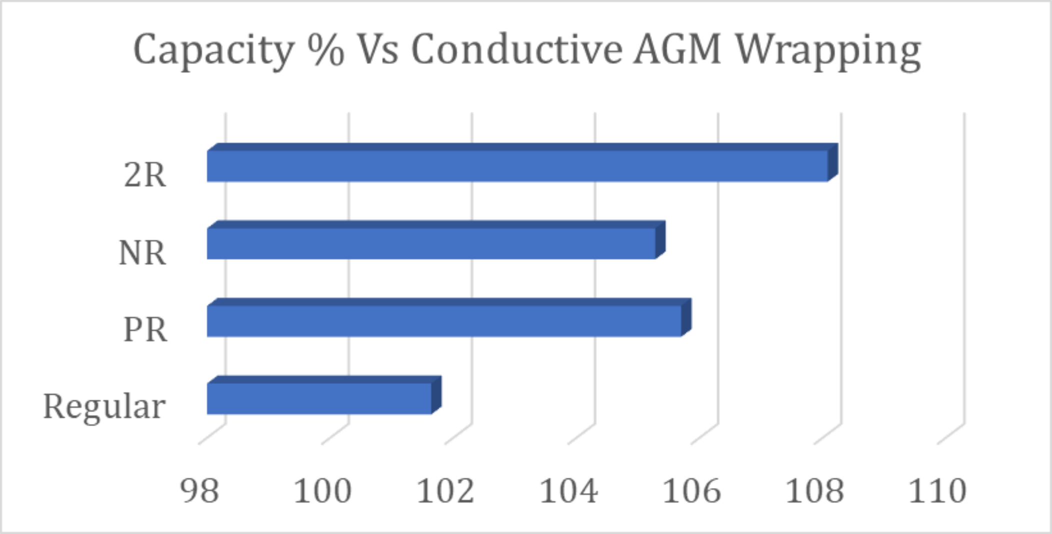


Fig. Process of coating the separator.



PR- Positive Coat wrapping**; NR-** Negative Coat wrapping**;**
2R- Both (+Ve &-Ve) Coat wrapping

<u>Inference</u>:
Successfully coated the separator with graphene and tested the cells (2V) by assembling. Cell with both sides' separator found to be better with one side

3. Analysis of Carbon as current collector grid (Preliminary Study: Replaced negative Lead Grid)

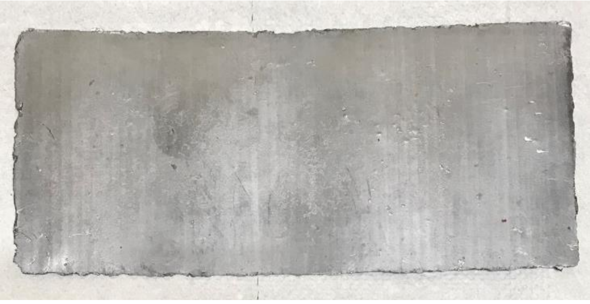
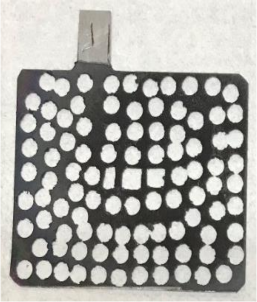


Fig. Pure Carbon sheet.

S. No.	Parameters	Regular (-Ve)	Trail
1	Base Element	Lead (Pb)	Carbon ©
2	Grid Weight (gm)	10	0.5

Carbon Grid



Regular Lead Grid

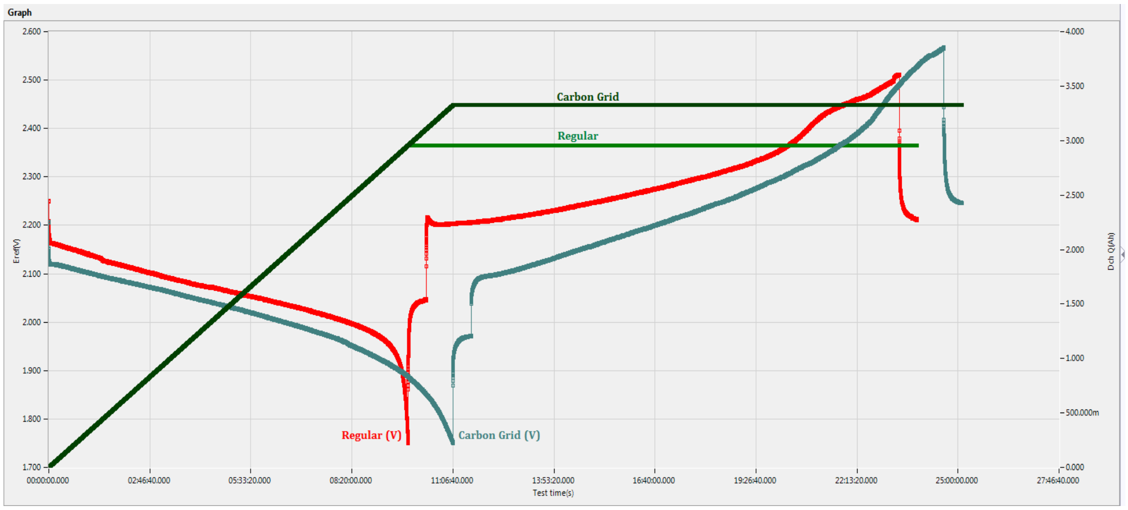


Fig. Capacity (C10) Discharge/Charging Profile of regular and caron grid cell.

Inference: Successfully replaced negative lead grid with carbon grid and found to be superior when compared to lead grid in C10capacity test.

Test	Requirement	Regular	Carbon Grid	Remarks
Capacity (C10)	≥95%	3.08(Ah); 103%	3.3 (Ah); 110%	~7% Improvement