SURFACE AND INTERFACE PROPERTIES – NANOSCALE DEVICE – THIN FILM BATTERY

A THESIS

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requirements for the award of the degree
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by
RAHUL GUPTA

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled ***Surface and Interface Properties – Nanoscale Device – Thin Film Battery*** in the partial fulfillment of the requirements for the award of the degree of **MASTER OF SCIENCE** and submitted in the **DEPARTMENT OF PHYSICS Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from July 2020 to June 2021 under the supervision of Dr. Sudeshna Chattopadhyay, Associate Professor, Department of Physics IIT INDORE. The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

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

June 18, 2021

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ABSTRACT

Batteries are becoming more widely used as portable and small electronic equipment increases, so does the use of various battery technologies. The increasing demands of a sustainable energy storage system being placed on batteries indicate that the battery technology has developed considerably in the past few years (since 1990), and more development can be expected in the future. Environmental concerns provide extra attention to this field as we have already harmed it enough in the recent past. Li-ion batteries mainly dominate the present battery market because of their long durability, good capacity, and temperature efficiency. But lithium is a very rare material, and that's why Li-ion batteries are not considered as sustainable source for the future demands. This motivates researchers to find new sustainable battery technologies. Al-ion, Na-ion, and K-ion are some examples of new battery technologies. Research for these battery technologies has already started all over the world, but much to do in this field to reach the desired objective.

Al-ion batteries are one of the promising solutions because of the availability of raw material and high theoretical specific energy density. To achieve its high theoretical capacity, we need to use aluminum metal as the negative electrode. For the better performance of the Al-ion battery system, we need to work to find suitable electrolyte material and positive electrode material.

In this thesis work, the performance of graphitized silicon carbide (EG/SiC) electrode systems, in view of their graphitization induced novel surface and interface properties, for Al-ion battery application has been explored using different techniques. In this work, our main focus is on the analysis of surface properties of positive electrode material by using two techniques, the cyclic voltammetry technique and the galvanostatic charge-discharge method. Graphitized SiC has been explored as a working electrode material in Al-ion battery application. It should be noted that previous studies show that such electrode exhibits good Li-ion intake capacity Li-ion battery applications. The cyclic voltammetry technique provides information about the redox reaction mechanism and durability of the battery system. And also, with the help of areas of the voltammograms, we can calculate the specific capacitance of the cell. The galvanostatic charge-discharge method is important for quantitative analysis as we can calculate specific charge

capacity, specific energy density, and power density of the system. Analysis of galvanostatic results also provide information about the resistivities faced by the ions due to the electrolyte and electrode-electrolyte interface. By using such relevant data analysis techniques, we can thoroughly study the effect of surface/interface properties in graphitized electrode system in comparison to the bare SiC electrode in determining the performance towards the Al-ion battery application.

It should be noted that the complete experimental part of this project work was carried out by the Ph.D. students of my supervisor's (Dr. Sudeshna Chattopadhyay) research group prior to the Covid 19 situation, and in this thesis work I have focused on the analysis and data interpretation of this project and included it accordingly in my thesis.

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Chapter 1

INTRODUCTION

If we look at the world's energy consumption for the last 100 years, we can see that it is drastically increasing as the human population and technology increase. We have been using non-renewable energy resources like coal, petroleum, natural gas, etc., but they have limitations in availability and many restrictions like environmental issues. One common question that anyone can think about is that what will happen if natural energy resources extent. So, the battery is one of the solutions for our future energy demand. Due to the considerable use of natural energy resources, we are facing problems like global warming, rising sea levels, and other steep changes in world climate. For the proper use of renewable energy resources like solar energy, geothermal energy, wind energy, and hydropower, we need a promising energy storage system that can store their energy and release it on demand.

A battery is a device that can store electric energy in the form of chemical energy. Batteries can be divided into two types:

1. Non-rechargeable batteries (primary batteries)
2. Rechargeable batteries (secondary batteries)

As their name suggests, primary batteries cannot be recharged once depleted, while secondary batteries can be recharged multiple times. The first primary battery was invented in 1800 by the Italian physicist Alessandro Volta, a Cu-Zn battery, and the first rechargeable battery was a lead-acid battery (in 1859). Generally, cell reactions decide the rechargeability of the batteries; if the cell reaction is reversible, then the battery system will be rechargeable, while in the case of the primary battery, cell reaction is irreversible. Fuel cells are also similar to batteries in that they produce an electric current but require the continuous addition of fuel. The most popular examples of primary batteries are Alkaline Batteries and Zinc-Carbon batteries. And there are many famous examples of secondary batteries like Lead-Acid battery, Nickel-Cadmium battery, and the most popular is the Li-ion battery. Novel aluminium ion battery is also an important example of secondary batteries. If we use solid electrodes and solid electrolytes instead of liquid or polymer gel electrolytes, this kind of battery is called the solid-state battery.

1.1 Battery and its components

Batteries are made up of three essential components: an anode, a cathode, and an electrolyte. The properties of these essential components directly affect the performance of the battery system. The electrode which releases electrons is generally called as negative electrode, and the electrode which acquires the electron is called positive electrode. An electrolyte is a medium that provides the ion transport mechanism between both the electrode.It is important to note that the electrodes in a battery are always made from two dissimilar materials (so never both from the same metal), which have to be conductors of electricity. This is the key to how and why a battery works: one of the materials "likes" to give up electrons, the other likes to receive them. There are some other components also like a separator, outermost insulating cover, and connectors, which also play their roles in the performance of a battery [1-2].

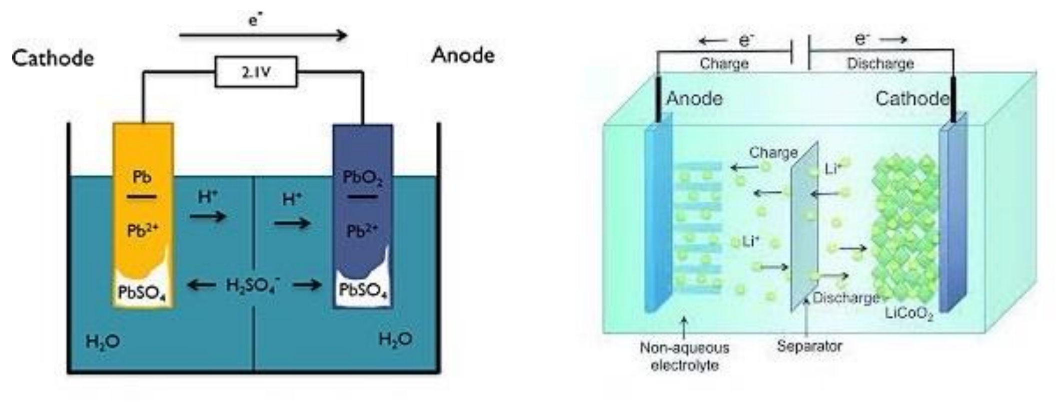


Fig. 1: (a) working of lead-acid battery; (b) working of Li-ion battery. [20]

1.2 Properties required for a good battery system

1. Single-cell voltage: a cell is a fundamental unit of a battery system. For voltage requirements, we need high single-cell voltage. For now, Li-ion batteries have the highest single cell voltage around 3.7 V. Single cell voltage = open circuit voltage – all resistivities

2. Specific energy: it is the product of the cell voltage and the specific capacity (how much energy it holds).

3. Long life character: long life means one can use the battery multiple times. It mainly depends upon the cell reaction. Some other important properties are it should be cost-effective, raw material availability, safety, and the battery should be environment friendly [1].

1.3 Modern battery technologies

Let's look at the current demands of batteries; we need essential battery systems for small electronic equipment like mobile phones, laptops, and medical devices, and especially when we look toward our environmental concerns, we need a promising energy storage system for motor vehicles. There are many battery technologies available, like lead-acid batteries, nickel-cadmium batteries, and Li-ion batteries. When we see the current demand for batteries, we need small-sized batteries with high specific energy and good durability. Currently, the Li-ion battery dominates the battery market due to its high single cell voltage, high specific energy, and long durability. Li-ion batteries have high single-cell voltages around 3–4 V and specific energy 100-265Wh/kg or 250-670Wh/L. The commercialization of Li-ion was started in 1991 by Sony and Asahi Kasei's team [2-3].

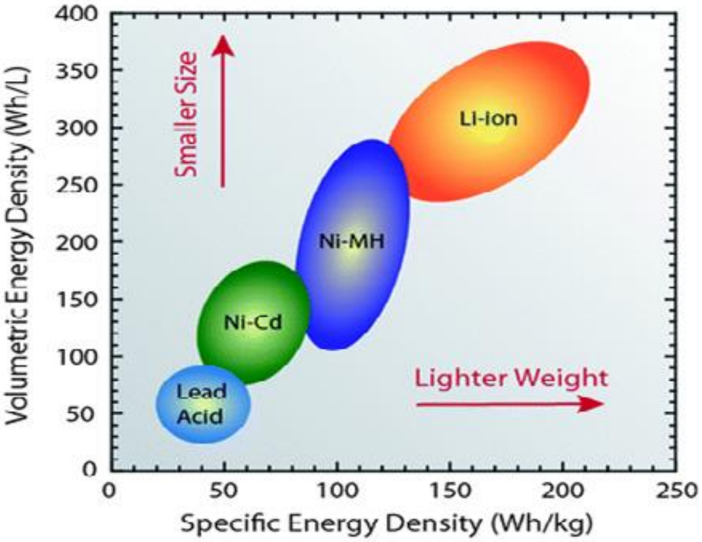


Figure 2 Comparison between different battery technologies [2]

Most of the new battery technologies are based upon thin-film technology. To construct a thin film battery, it is necessary to fabricate all the battery components, as an anode, a solid electrolyte, a cathode, and current leads into multi-layered thin films by suitable techniques. There is a demand for other battery technologies like Na-ion battery, K-ion battery, and Al-ion battery.

When we see statistics of different organizations, we can understand why research work in this field is one of the hottest research topics. Data from many universities and different policies of governments suggest that the demand for batteries for various sectors will increase drastically in the future. As we know, today, most of the use of Li-ion batteries is in the sectors of electric vehicles, smart electronic devices, and the field of renewable energy. And demand in these sectors will increase in the future, so we need new battery technologies like Al-ion batteries, K-ion, and Na-ion batteries.

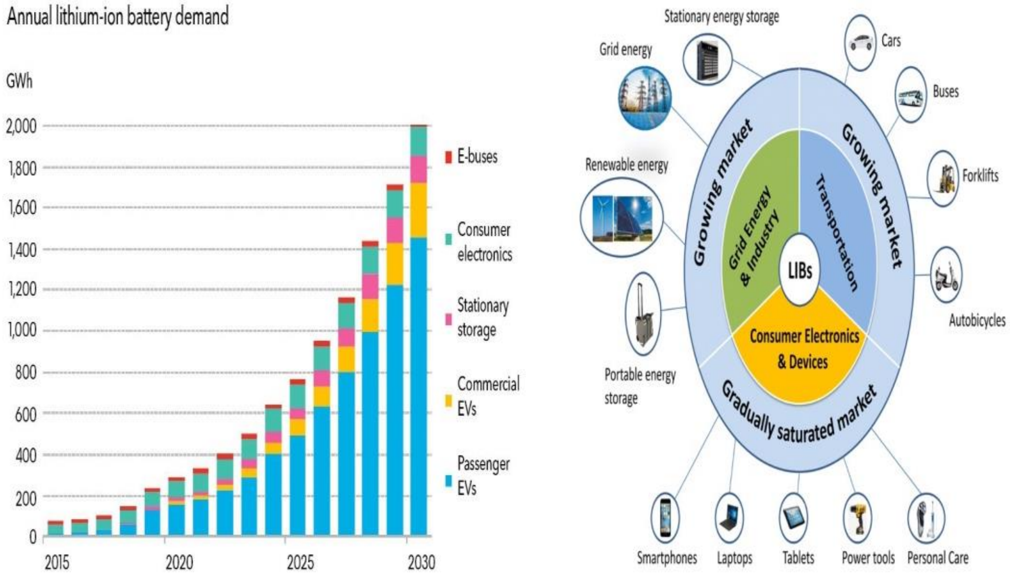


Fig. 3(a) annual demand of Li-ion batteries; (b) demand for modern batteries in different sectors [2]

1.1 Comparative study of different battery technologies

Li-ion battery, lead-acid battery, nickel-cadmium battery, and nickel-metal hybrid battery are the types of batteries we mainly use. And Li-ion battery covers around 60% battery market worldwide. The first major issue regarding Li-ion batteries is that lithium as raw material is very rare, which is also costly. Lithium constitutes around 0.0002 percent of the earth's crust, while aluminium and sodium constitute 8.23% and 2.36% of the earth's crust, respectively [4-5]. Significant issues with lead-acid batteries are their heavyweight and burning problems. There are issues like the burning of batteries during fast charging, less durability, high maintenance cost, low specific energy, and low value of single-cell voltage, motivating our researchers to find new battery technologies.

Table 1 properties of different battery systems [2]

Properties	Li-ion battery	Ni-Cd battery	Lead-acid battery	NiMH
1.Specific energy density(Wh/kg)	110-160	45-80	30-50	60-120
2.Cell voltage(volt)	3.6	1.25	2	1.25
3.Cycle life	500-1000	1500	200-300	300-500
4.Operating temperature (Celsius)	-20 to 60	-40 to 60	-20 to 60	-20 to 60
5.Self discharge(27C)	10%	20%	5%	30%
6.Fast charging	2-4h	1h	8-16h	2-4h

Therefore, the search for new batteries will become increasingly important in the future to diversify battery technologies. But the question here arises that which materials seem promising? Using a selection algorithm to evaluate suitable materials, the concept of a rechargeable, high-valent all-solid-state aluminum-ion battery appears good, in which metallic aluminum is used as the negative electrode. On the one hand, these batteries offer the advantage of a (theoretically) four times higher volumetric capacity compared to lithium-ion batteries. On the other hand, aluminum is the most abundant metal in the earth's crust. There is a mature industry and recycling infrastructure, making aluminum very cost-efficient [5]. This would make the aluminum-ion battery a vital contribution to the energy transition process, already started globally. So far, it has not been possible to exploit this technological potential, as suitable positive electrodes and electrolyte materials are still lacking. The discovery of inorganic materials with high aluminum-ion mobility—usable as solid electrolytes or intercalation electrodes—is a necessary innovation leap forward in the field of rechargeable high-valent ion batteries. It is also important to find suitable electrode materials for aluminum ion batteries. In this thesis work, I have analyzed the performance of graphitized silicon carbide (EG/SiC) electrode systems, in view of their novel surface and interface properties, for Al-ion battery application using different techniques.

Chapter 2

THEORETICAL BACKGROUND

We have been using different electrode materials for various battery technologies like different carbon electrode materials, metal oxides, and many others. It is necessary to analyze the properties of good electrode materials. We are using examples from electrode materials that we have been operating in various battery technologies to understand which materials would be helpful in Al-ion batteries.

1.1 Aluminium ion battery and its types: In the literature, the term "aluminum-ion battery" is used for various systems applying aluminum. But in this thesis work, we restrict to a definition pointed out by Kravchyk et al., 2017, an "aluminum-ion battery" characterized by a unidirectional flow of Al (+3) ions from one electrode to the other. To exploit an aluminum-ion battery's high theoretical energy densities (13.36 Wh/cm3, which is 1.6 times higher than gasoline14 of 8.6 Wh/cm3), a metallic negative electrode made of pure aluminum needs to be used [5].

It can be divided into various types:

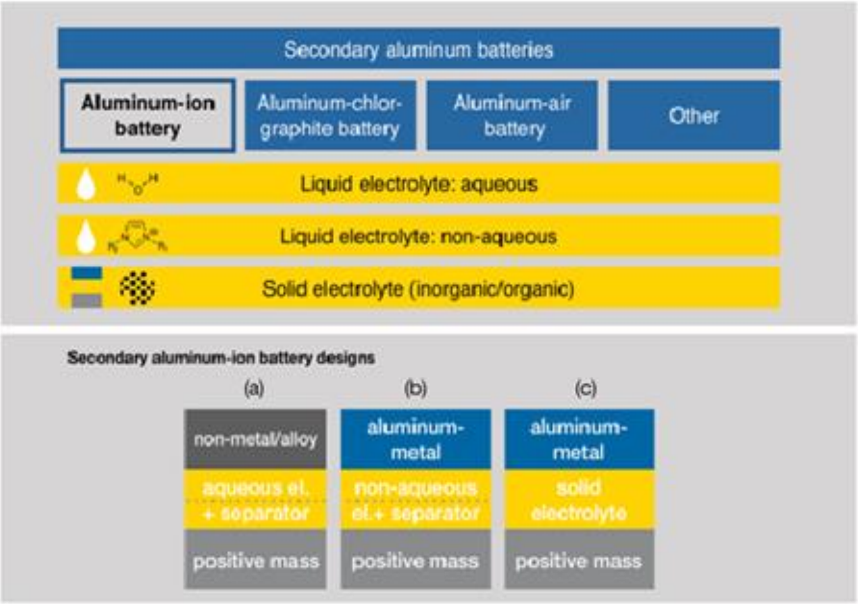


Figure 4 different types of Al-ion batteries [5]

Table 2 advantages and disadvantages of aluminium as negative electrode [5]

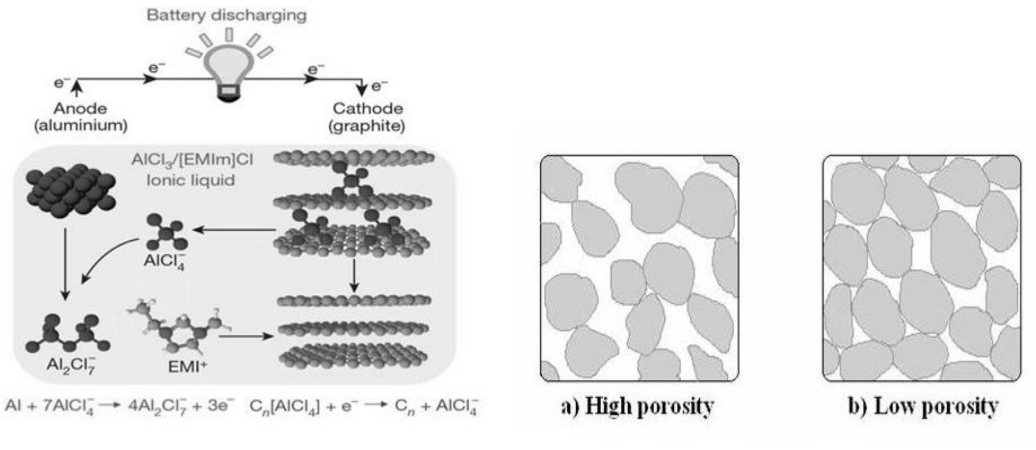
Advantages	**Disadvantages**
Energy density: Volumetric capacity is four times higher than for lithium.	Electrochemical window: Difficult to find liquid electrolytes, which enable dissolution and plating of elemental aluminum.
Environment: Not harmful, environment-friendly, less electrical energy necessary for producing metallic aluminum (as negative electrode), less soil needs to be moved during mining due to higher concentrations.	Coulomb interaction: High-valence state of+3 may introduce slow intercalation/deintercalation kinetics and ion conduction.
Infrastructure: Matured and already well-established production, electroplating, manufacturing, recycling, and scrap collecting infrastructures are available.	Redox potential: With –1.67 V relatively low compared to lithium.
Resources/prize: Small political supply risk, distribution of production and recycling plants worldwide, small price due to very high abundance.	High oxygen affinity: Influence on environmental conditions and small changes in the local chemistry.
Safety: Does not ignite in air, ensuring greater safety of corresponding cells and ease of processing.	Research efforts: Not intense; in the beginning, 30 years delay in comparison to lithium.

1.2 Properties and challenges of electrode materials:

1 Specific charge capacity: this property depends upon how much charge an electrode can hold (per unit mass). If material is good enough to hold the charge in its structure, it will be a promising electrode material for a high specific energy battery system.

2. Less reactive: the electrode material should be stable in ambient conditions and should not react with the electrolyte used in the battery. For better durability of the battery system, this property is essential.

3. Thermal stability: thermal stability of the material is required to use the battery at different temperatures and for safety purposes.
4. Volume expansion: during intercalation (process of inserting ions in host materials) process the volume of the electrode material varies. Generally, we use layered structure materials for the intercalation process, but the volume change is very large; that's why these materials are not suitable for a stable battery system (fig 5a).
5. Cost and availability are also essential factors in the selection process of electrode material.
6. High single voltage is important for specific energy of the battery system so, the material should provide high single-cell voltage.
7. Porosity: it is defined as the ratio of pore volume to the whole nominal volume of a body (fig. 5b). Porosity also depends on the electrode material's manufacturing pressure; as porosity decreases, energy density increases because when porosity is less, then the electrode is insufficiently wetted by the electrolyte.



a) High porosity

b) Low porosity

Figure 5(a) working of aluminium ion battery [21]; (b) porosity of material

SEI layer (solid electrolyte interface): layer formed due to oxidation and reduction of the electrolyte near the electrodes is called solid electrolyte interface. The SEI layer has a vital role in terms of cycle life limitations, capacity for reversibility and safety, and in the functioning of a battery system. Atomic Layer Deposition (ALD) coatings are beneficial to improve the well functioning of the batteries by stabilizing or preventing the SEI layer.

The formation of the SEI layer is a fundamental factor in the design and functioning of high-performance batteries. The primary role of the SEI layer is the prevention of further electrolyte decomposition to maintain cycling ability. This requires that the SEI layer is well adhered to the electrode material, has good electronic insulation properties, and can conduct positive ions [6].

Interfacial reactions on the surface particles of both electrodes affect the performance of positive ions through the SEI layer. The irreversible reactions near the surface of electrodes will increase the thickness of the SEI layer and directly affect the performance of the battery.

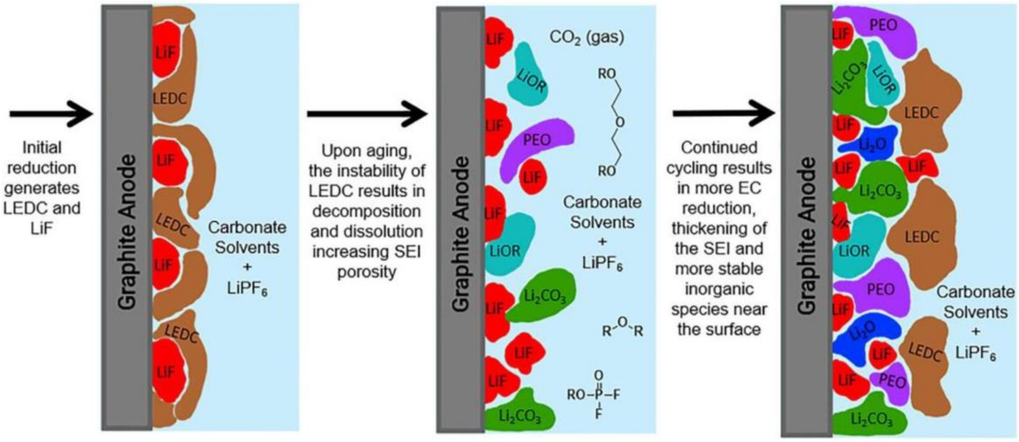


Figure 6 SEI layer formations [22]

So, analyzing surface properties is one of the crucial parts of the battery research works. This thesis will analyze some surface properties of SiC electrode systems with coating and without coating for aluminium ion batteries.

Chapter 3

Techniques Used

It should be noted that the complete experimental part of this project work was carried out by the Ph.D. students of my supervisor’s (Dr. Sudeshna Chattopadhyay) research group prior to the Covid 19 situation, and in this thesis work I have focused on the analysis and data interpretation of this project and included it accordingly in my thesis.

A comprehensive assessment of a certain electrode material includes energy/power density, conversion efficiency, and calendar lifespan. The determination of these factors involves characteristic parameters such as voltage, current, capacity, and testing duration that can be directly collected from electrochemical analysis. Cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) are the two most popular testing techniques. Both methods offer information on the voltage and energy profiles of the tested materials. In the first technique, we record the current response at different applied voltages (cyclic voltammetry); in the latter, we monitor the time-resolved voltage evolution under certain forced currents (galvanostatic measurement).

3.1 Cyclic voltammetry: Cyclic voltammetry (CV) is a powerful and advantageous electrochemical technique commonly employed to investigate the molecular species's reduction and oxidation processes. CV is also invaluable to study electron transfer-initiated chemical reactions, which includes catalysis. In this technique, we analyze graphs between current and voltage; these graphs are called voltammograms or cyclic voltammograms. The x-axis represents applied potential (E) while the y-axis is the response; here the resulting current (i) passed. One crucial parameter is scan rate; it indicates that the potential varied linearly at some speed during the experiment [7-9].

3.1.1 Experimental setup: The vessel used for acyclic voltammetry experiment is called an electrochemical cell. A schematic representation of an electrochemical cell is presented in figure 7.

Working Electrode: The working electrode carries out the electrochemical event of interest. A potentiostat is used to control the applied potential of the working electrode as a function of the reference electrode potential. The most important aspect of the working electrode is that it is made up of inert redox material in the potential range of interest. Because the electrochemical event of interest occurs at the working electrode surface, it is necessary that the electrode surface be extremely clean and its surface area well-defined. In our experiment, we are using two different working electrodes, bare SiC and EG/SiC.

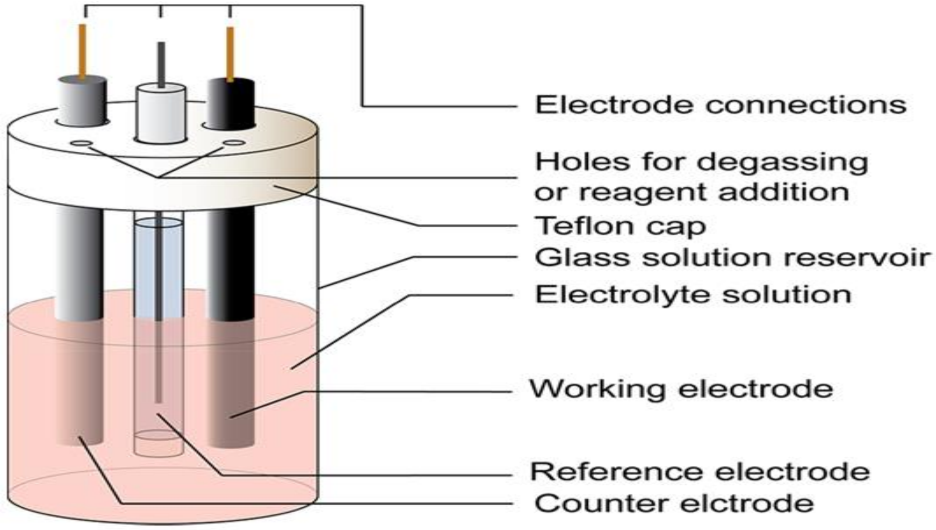


Figure 7 experimental setup of CV [7]

Reference Electrode: A reference electrode has a well-defined and stable equilibrium potential. It is used as a reference point against which the potential of other electrode scan be measured. The applied potential is thus typically reported as a specific reference. Some common reference electrodes used in aqueous media include the saturated calomel electrode (SCE), standard hydrogen electrode (SHE), and the AgCl/Ag electrode.

Counter Electrode: The purpose of the counter electrode is to complete the electrical circuit. Current is recorded as electrons flow between the WE and CE.

3.1.2 CV graph explanation for reversible redox reaction: figure 8 H represents the CV curve, and I is the graph of applied potential with time, while graphs A to G are the graphs of concentration of reduced (green) and oxidized (blue) part as a function of distance from the electrode [7].

3.1.3 Qualitative analysis by using CV technique: we can divide the complete CV graph into two parts first from point A to D, and second is from point D to G. The Nernst equation gives a powerful way to predict how a system will respond to the change of concentration of species in solution or a change in the electrode potential. Nernst's equation relates the potential of an electrochemical cell (E) to the standard potential (E) of a species and relative activities of oxidized and reduced analyte (concentrations) in the system at equilibrium.

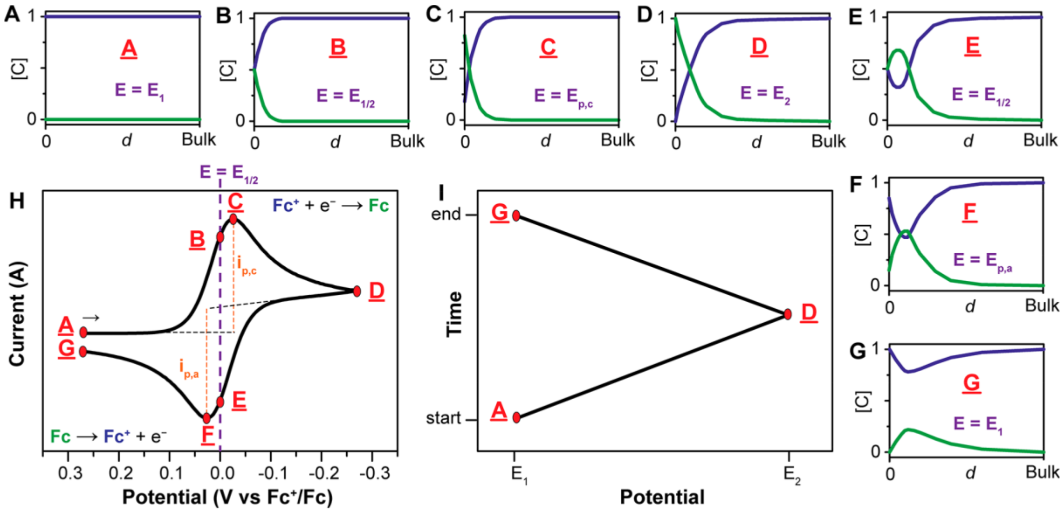


Figure 8 CV diagram of reversible redox reaction [7]

$$E = E^0 + \frac{RT}{nF} ln \frac{ox}{red} \qquad \text{(Nernst's equation)}$$

In the equation, F is Faraday's constant, R is the universal gas constant, n is the number of electrons, and T is the temperature. The formal potential is specific to the experimental conditions employed and is often estimated with the experimentally determinedE1/2 value (figure 8, average potential between points F and C in panel H).When the potential is scanned during the cyclic voltammetry experiment, the concentration of the species in solution near the electrode surface changes following the Nernst equation. As the potential is scanned negatively from point A to point D, positive ions are steadily depleted near the electrode as it is reduced to an atom or molecule. At point C, where the peak cathodic current is observed, the current is dictated by the delivery of additional positive ions via diffusion from the bulk solution. The volume of solution at the surface of the electrode containing the reduced atoms, called the diffusion layer, continues to grow throughout the scan. This slows down the mass transport of positive ions to the electrode. Thus, upon scanning to more negative potentials, the rate of diffusion of positive ions from the bulk solution to the electrode surface becomes slower; resulting in a decrease in the current as the scan continues (C → D). When the switching potential (D) is reached, the scan direction is reversed, and the potentials scanned in the positive direction. While the concentration of positive ions at the electrode surface was depleted, the concentration of reduced atoms at the electrode surface increased, satisfying the Nernst equation. Reduced atoms present at the electrode surface are oxidized back to positive ions as the applied potential becomes more positive. The two peaks are separated due to the diffusion of the analyte to and from the electrode. If the reduction process is chemically and electrochemically reversible, then the difference between anodic and cathodic peak potentials is called peak-to-peak separation (ΔEp). But maximum electrochemical reactions are irreversible in nature [7-8].

CV curves of irreversible or quasi irreversible reactions are more complicated than the previous simple case.

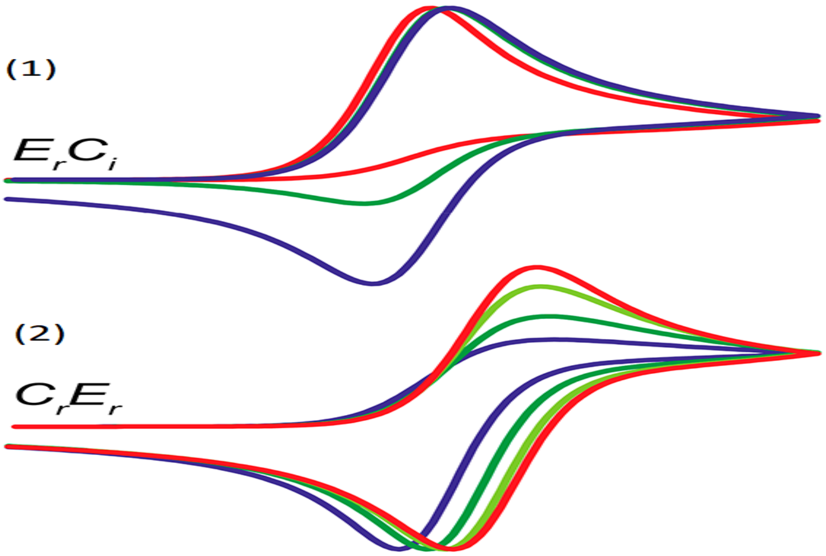


Figure 9 CV diagrams of irreversible redox reactions [7]

EC Coupled ReactionE_rC_i: (Reversible Electron Transfer Followed by an Irreversible Homogeneous Chemical Reaction) in this reaction, a simple reduction reaction is followed by the irreversible chemical reaction.

$$Ox + e^- \leftrightarrow Red$$
$$Red \rightarrow Z$$

CE Coupled ReactionC_rE_r: (Reversible Chemical Step Followed by a Reversible Electron Transfer) In this example, the amount of Ox available for the reduction is dictated by the equilibrium constant of the first step. The greater the equilibrium constant, the more reversible the voltammograms.

$$Z \leftrightarrow Ox$$
$$Ox + e^- \leftrightarrow Red$$

In the cases of irreversible redox reactions, the CV diagrams are more complicated. Still, they provide important information regarding the cycle life of the battery and side reactions near the surface of the working electrode [7-8].

3.1.4 Quantitative analysis: although the cyclic voltammetry technique is best at providing qualitative analysis of reaction mechanisms, we can also calculate some necessary quantities like specific capacitance, energy density, power density, specific capacity.

Specific capacitance:

$$C = \frac{q}{V} \tag{1}$$

$$C = \frac{It}{V} \tag{2}$$

$$C_P = \frac{I}{mK} \tag{3}$$

(Where m is mass, K is scan rate and C_P is specific capacitance)

$$\int_{V_1}^{V_2} I(V)dV = \int_{V_1}^{V_2} C_P mK\, dV \tag{4}$$

$$A_1 = C_P mK(V_2 - V_1) \tag{5}$$

$$A_2 = C_P mK(V_1 - V_2) \tag{6}$$

$$A = A_1 - A_2 = 2C_P mK(V_2 - V_1) \tag{7}$$

$$C_P = \frac{A}{2mK(V_2 - V_1)} \tag{8}$$

Energy density $E = \frac{1}{2} C_P (V_2 - V_1)^2$(Wh/kg)

Power density $= \frac{E}{dt}$ (W/kg)

Specific capacity= $\frac{Idt}{m}$ (Ah/gm)

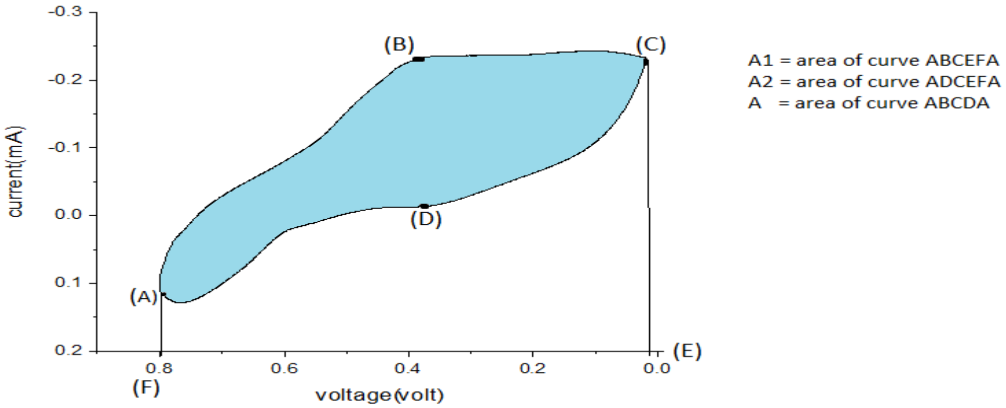


Fig. 10 area of CV curve

3.2 Galvanostatic method: Galvanostatic charge-discharge measurements record the voltage response under the constant applied current. It is the most practical method to assess the capacity, reversibility, stability, and rate capability of electrode materials. By repeatedly charging/discharging batteries, we can evaluate the cycle life, often referred to as the cycle number, when the reversible capacity becomes 80% of its initial value. The cycle number is probably the most crucial parameter for rechargeable batteries, as their service time is expected to be very long.

3.2.1 Experimental setup: It is also a three-electrode measurement system like cyclic voltammetry, where we analyze the time vs. potential graphs. For galvanostatic analysis, first constant current is provided, and then we analyze different charging-discharging cycles of the system. Its experimental setup is similar to the cyclic voltammetry technique.

3.2.2 Quantitative analysis: galvanostatic analysis method is more suitable for quantitative analysis because, in this method, we can do important calculations for a large number of cycles and compare them. This method provides quantitative information about the electrode like we can calculate specific charge capacity, specific capacitance, specific energy density, and power density of the system.

1. Specific charge capacity: how much charge a material can hold is called specific charge capacity.($\frac{I\Delta t}{m}$ mAh/gm)
2. Specific capacitance (C) = $\frac{I\Delta t}{m\Delta V}$ F/gm

3. Specific energy density = $\frac{1}{2}C\Delta V^2$Wh/kg
4. Specific power density = $\frac{E}{\Delta t}$ W/kg

We can calculate these values from this method and compare them with the cyclic voltammetry technique. This will lead to more authenticity of our conclusions for any electrode system [10].

3.2.3 Qualitative analysis: Although the cyclic voltammetry technique is best at providing information about redox reactions mechanism, we can also analyze these properties from the galvanostatic charge-discharge method. The first property that we can understand from the GS method is the cyclic efficiency of the battery. The difference between the times taken during the discharging process for different cycles shows the cyclic efficiency of the battery system [9-10].

The second important thing that we can see in the galvanostatic method diagrams (figure 11) is the potential drop during the discharging process [11].

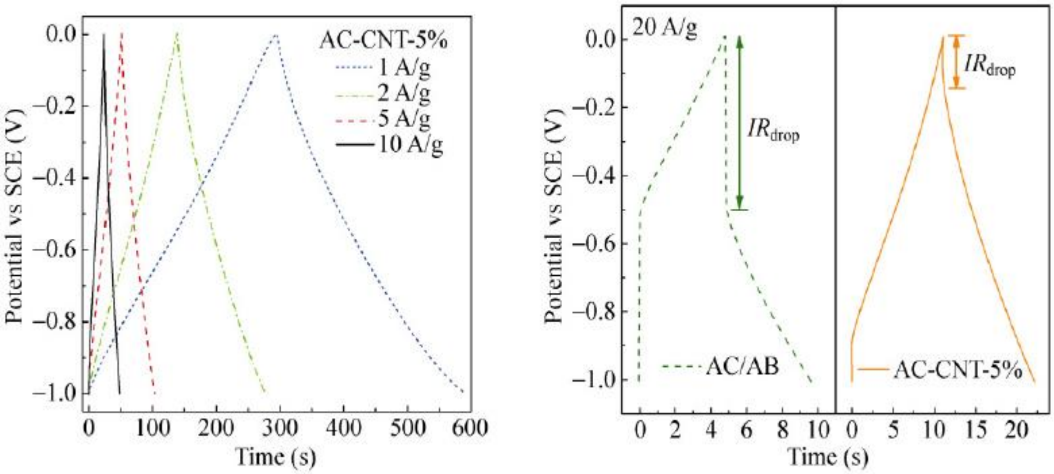


Figure 11 potential drop of carbon paper electrodes [11]

The reason behind the potential drop in discharging process is the resistance faced by the ions due to the electrolyte and electrode-electrolyte interface. If the size of the solid electrolyte interface increases, then resistance will increase, and it will result in the enhancement of IR drop. Due to the sizeable potential drop, the time taken during the discharging process will decrease, and as we know from the quantitative analysis, the values of specific charge capacity and energy density will decrease. A small IR drop is required for good battery technology.

Chapter 4

Results and Discussions

In this thesis, the performance of graphitized silicon carbide (EG/SiC) electrode systems, in view of their graphitization induced novel surface and interface properties, for Al-ion battery application has been explored using different techniques. Important properties of two working electrodes, bare silicon carbide (SiC), and epitaxial graphene/SiC (EG/SiC) are explained by using the relevant techniques. First, by using the cyclic voltammetry technique, the redox reaction mechanism is discussed for both electrodes. Comparative analysis for both materials is also discussed to see the difference created by surface modification of SiC by epitaxial graphene. Then, some calculations regarding specific capacitance and specific energy density are done using the galvanostatic data analysis method. Here we are using epitaxial graphene for surface modification because the layering of graphene will help in increasing its volumetric energy density and also its cyclic ability. As it is well known, graphene is one of the most stable materials; that is why layering of graphene will decrease the side reactions near the electrode (between electrolyte and electrode), and that is how it will increase its cyclic ability, which is a fundamental property for a good rechargeable battery system. Graphene layering has the potential to increase the temperature efficiency of the electrode. We already know that for Li-ion battery, graphene layered SiC electrode has high stability, good volumetric energy density, and good cyclic ability [12-14].

4.1 Cyclic voltammetry analysis of bare SiC WE: In the cyclic voltammetry technique, we analyze the redox reaction mechanism by using a current versus voltage graph. In this experiment, the potential is scanned at the scan rate of 0.2mV/sec, and the potential window is 0 - 0.8V.

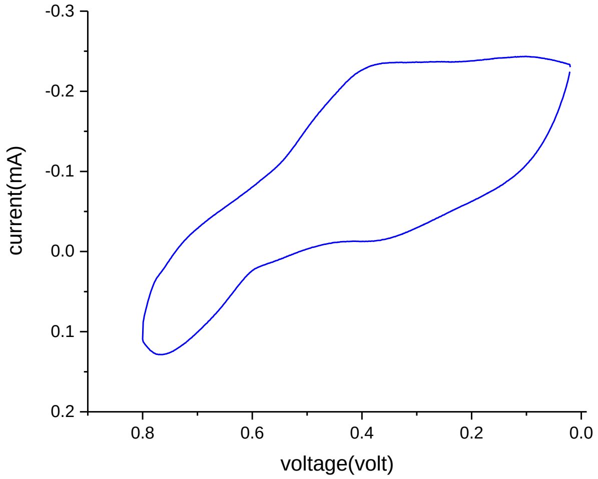


Figure 12(a) CV diagram for 2nd cycle (bare SiC electrode)

First, the potential is scanned negatively from 0.8V to 0V. In this negative scan, the current rises up to a certain point (cathodic peak) due to the diffusion of ions, then decreases as a normal CV diagram of a reversible reaction. But current value increases again after achieving the cathodic peak value (fig 12(C)). We can explain this by the double-layer capacitance concept.In the double-layer capacitance or pseudo capacitance phenomenon (fig. 12(b)), the former rise is due to the diffusion current of reversible electrolyte ions adsorbed at the interface between the electrode and electrolyte, while the latter arises due to the sequential redox reactions that occurred at the electrode surface. So we can say this in the CV diagram of bare SiC working electrode later rise in current is due to the sequential redox reactions at the surface of the electrode. This indicates the high charge capacity. So, it will be a good electrode in terms of charge capacity [15-16].

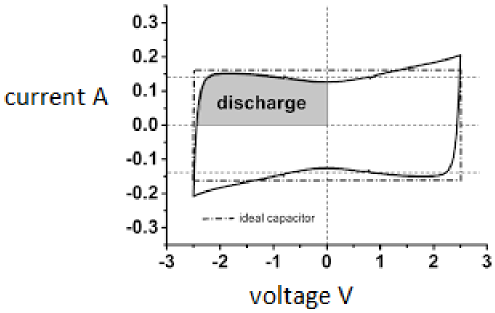


Figure 12(b) diagram of pseudo capacitance [15]

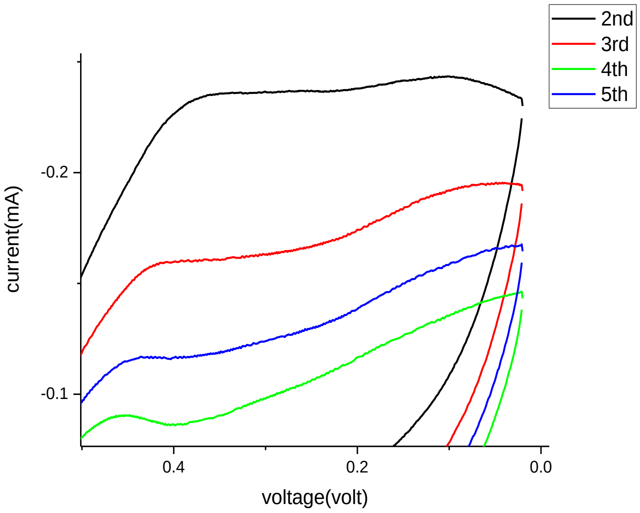


Figure 12(c) CV diagram of bare Sic WE for pseudocapacitance

The second difference in the above diagram is that the current value is not decreasing after achieving the anodic peak value, but it increases sharply (fig 12(d)). So the graph deviates from the normal rectangular shape during the oxidation process. From this sharp increase, we can predict that some other oxidation processes occur near the electrode surface after a certain potential is reached during the oxidation process [17].

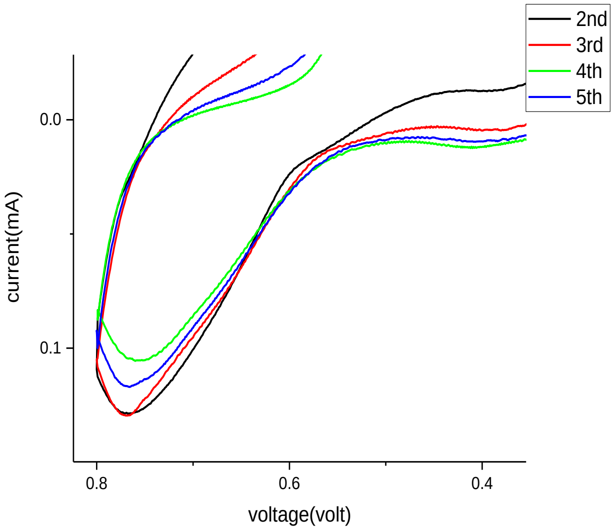


Figure 12(d) CV diagram for sharp increase in current

The next important thing that we can see in the cyclic voltammetry diagram of comparative analysis of different cycles (figure 2(e)) for bare SiC working electrode is that after each cycle, the values of cathodic and anodic peak current decreases. This explanation is important for analysing the cyclic efficiency of the rechargeable battery system. The change in the values is large in the CV diagram of the bare SiC working electrode, which indicates the irreversible redox reactions near the electrode surface. This large change in anodic and cathodic peak values will affect the battery performance directly. So, we need to minimize these irreversible side reactions. Also, the difference between anodic and cathodic peak values (in the opposite direction) for a particular cycle shows the irreversible redox reactions [7]. Epitaxial graphene can help increase the cyclic efficiency of the electrode because graphene is one of the most stable materials on the earth. Also, the layering of graphene has shown promising results for other electrode systems of different battery technologies.

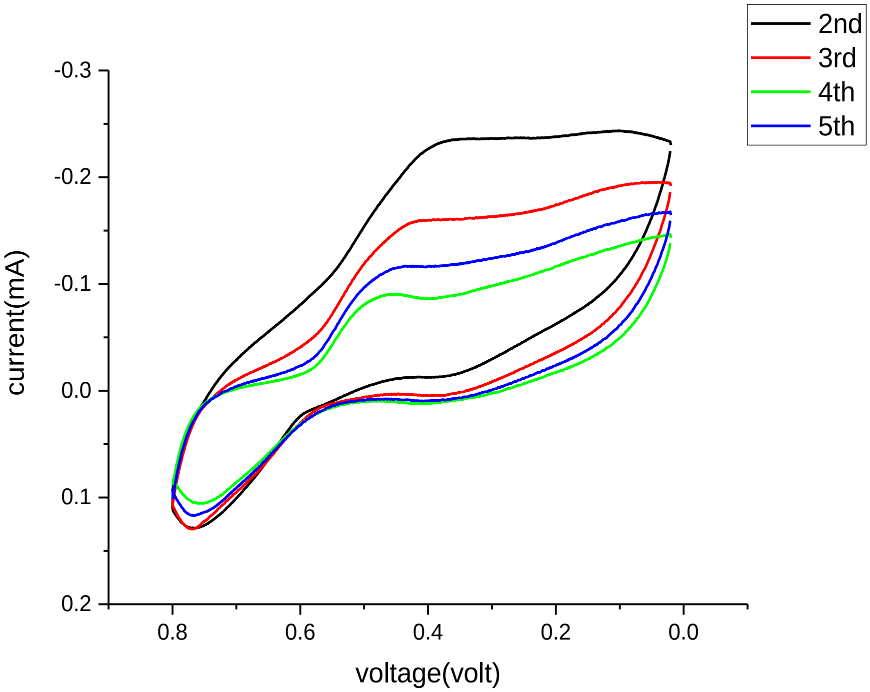


Figure 12(e) comparison of different CV cycles

Table 3 data for analyzing different CV diagrams of bare SiC WE

Cycle Number	**Current at cathodic peak(micro amp.)**	**Voltage at cathodic peak (mV)**	**Current at anodic peak(micro amp.)**	**Voltage at anodic peak (mV)**	**Area of CV curve (micro amp. V)**
2nd	-232	376	12	384	116
3rd	-157	421	4	382	914
4th	-116	439	8	370	756
5th	-095	453	9	413	645

4.2 Galvanostatic method for bare SiC WE: We are using a constant current 4.7 mA/gm for the galvanostatic charge-discharge method.

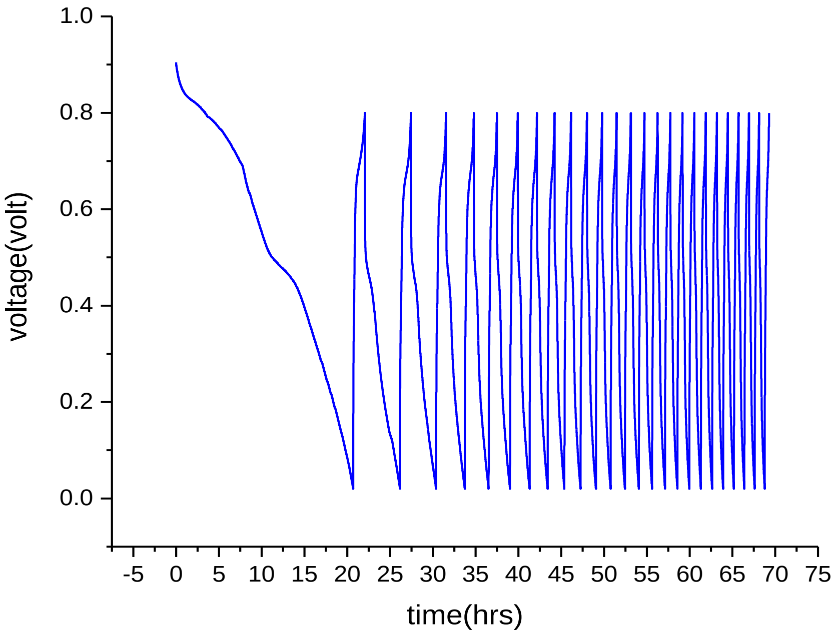


Figure 13(a) galvanostatic measurement diagram of bare SiC WE

The first thing that we can observe from the above diagram is after each charging-discharging cycle time taken for charging and discharging decreases. This indicates that somehow charge is consuming during a charge-discharge cycle, and that is why time taken by the battery is decreasing after each cycle. So it will affect the cyclic efficiency of the battery, which is a very important characteristic of a good rechargeable battery system. The cyclic voltammetry analysis also tells us about its cyclic efficiency, and the same results are shown by the galvanostatic charging-discharging method. So there is a requirement to minimizing its irreversible redox reactions to increase the cyclic efficiency of the battery system. The second important in the graph is sudden potential drop during the discharge cycle (figure 13(b)). The reason behind this potential drop is the resistance faced by the ions due to electrolyte and due to the electrode-electrolyte interface, which increases as the size of the SEI layer increases after each cycle [9-10]. And we can also understand this potential drop by the energy spent during the charging cycle is higher than the discharging cycle.

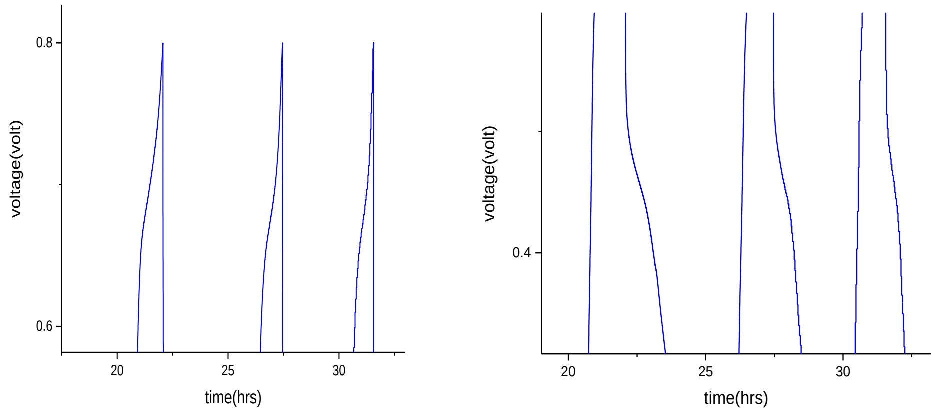


Figure 13(b) potential drop; (c) plateau-like structures

We can see the plateau-type structures in the discharging cycles. These kinds of structures occur at potentials where two phases, ion rich phase and ion poor phase, occur in the active material simultaneously. In other words, these plateaus occur at redox potentials of active material due to intercalation and deintercalation [9-10].

Some important calculations: by using this method, we can easily calculate the values of specific charge capacity, specific capacitance, specific energy density, and power density of the system.

Table 4 calculations of galvanostatic charge-discharge method (bare SiC)

Cycle number	Specific charge capacity (mAh/gm)	Specific capacitance(F/gm)	Specific energy density (mWh/gm)	Specific power density(mW/gm)
2nd	6.86	8.58	2.58	0.63
3rd	6.71	8.39	2.52	0.85
4th	5.92	7.41	2.23	1.03
5th	5.25	6.57	1.97	1.12

We can conclude from the above data that after each cycle, the value of specific charge capacity is decreasing in large amounts and also its energy density. To solve these problems, we will analyze the EG/SiC working electrode properties for the novel aluminium ion battery.

4.3 cyclic voltammetry analysis of EG/SiC WE: Here, we are using epitaxial graphene-coated SiC as the working electrode, and the scan rate of the experiment is 0.2mV/sec and the potential window is 0-0.8V.

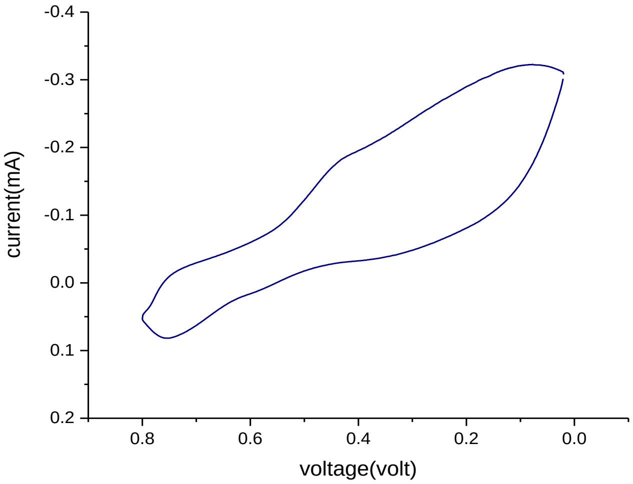


Figure 14(a) CV diagram of EG/SiC WE (2nd cycle)

When potential is scanned negatively, then the first current rises to a cathodic peak, and also after achieving this peak value, the current rises again, which can be explained by double-layer capacitance and sequential redox reactions near the surface of the electrode. But when we compare these two graphs, the rise in current is more in the case of EG/SiC WE than the bare SiC. And voltammogram is more close to the rectangular shape than the bare SiC case. This indicates the high charge capacity of the electrode, and this property is important for a good battery system. In the oxidation process, first, we get an anodic peak, and the current rises again. Another good thing about this CV diagram is the sharp rise in current is missing. In contrast, the CV diagram of bare SiC WE (figure 12(d)) showed a sharp increase. The difference between anodic and cathodic peak values for different cycles is less in the CV diagram of EG/SiC WE than the bare SiC. This also indicates less irreversible redox reactions than the previous case. In the case of EG/SiC working electrode, the cyclic efficiency of the battery will be good in comparison to bare SiC working electrode; this suggests that coating of graphene helped in increasing the performance of the aluminium ion battery system. But more research is required to get a better electrode system for rechargeable aluminium ion batteries.

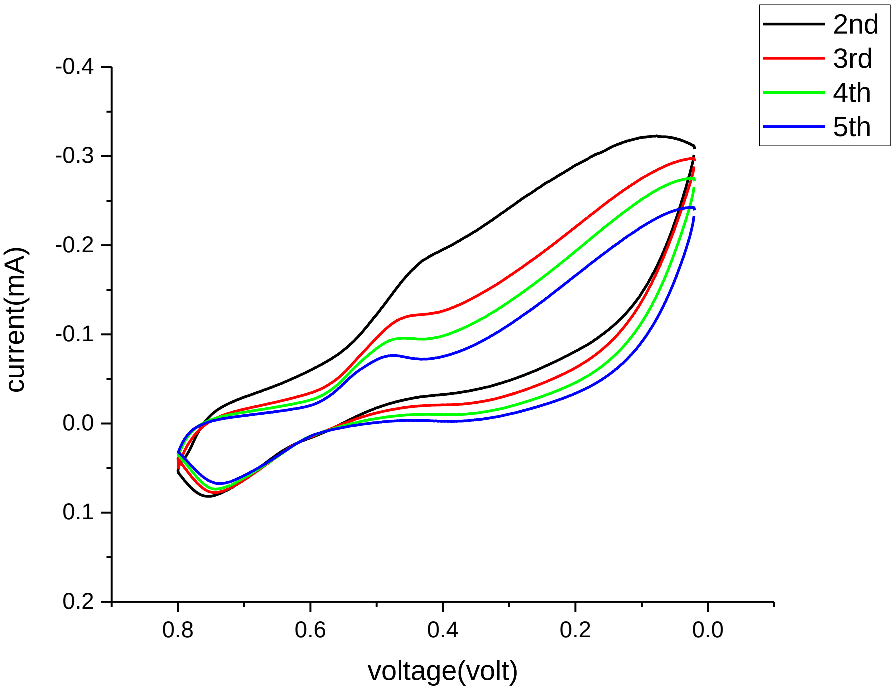


Figure 14(b) comparative study of CV diagrams for different cycle (EG/SiC WE)

Table 5 data for analyzing different CV cycles of EG/SiC WE

Cycle No.	**Current at cathodic peak (micro amp,)**	**Voltage at cathodic peak mV**	**Current at anodic peak (micro amp.)**	**Voltage at anodic peak mV**	**Area of CV curve (micro amp. V)**
2nd	-185	425	-33	388	104.5
3rd	-119	456	-21	385	77.5
4th	-95	468	-9	391	71.4
5th	-75	480	-2A	394	63.4

4.4 Galvanostatic analysis of EG/SiC WE: For the galvanostatic charging-discharging method, the value of constant current is 5.87mA/gm, and potential fluctuates between 0-0.8V.

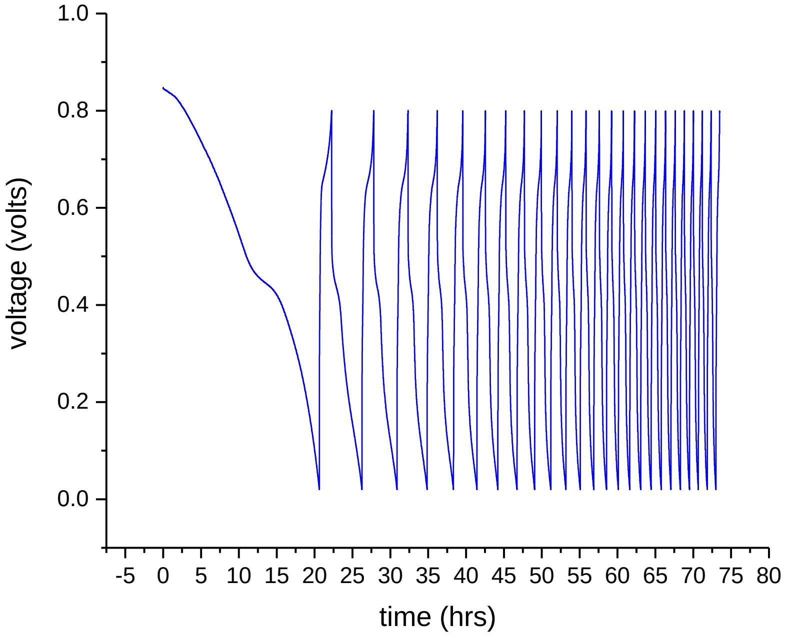


Figure 15(a): galvanostatic measurement diagram of EG/SiC WE

The first improved characteristic is the small less value of potential drop. As we know, potential drop during the discharging process is due to the resistance faced by the ions because of the electrolyte and SEI layer. So we can conclude that resistance faced by the ions in the case of EG/SiC WE is small in comparison to bare SiC WE. This will improve the performance of the battery system. The second important thing is the time taken for discharging initial cycles is more in EG/SiC galvanostatic analysis than the bare SiC. And as we know, specific charge capacity and specific capacitance are directly proportional to the time taken during the discharging process; that's why values of specific energy density and specific charge density will be high in the case of EG/SiC working electrode. If we compare the initial cycles of both the systems, then it is clearly visible that cell with EG/SiC WE has better performance than the bare SiC system. All these results explain that the layering of graphene helped in improving the performance of the electrode and the aluminium ion battery system.

Some important calculations:

Table 6 calculations of galvanostatic charging-discharging method (EG/SiC)

Cycle number	**Specific charge capacity(mAh/gm)**	**Specific capacitance(F/gm)**	**Specific energy density (mWh/gm)**	**Specific power density(mW/gm)**
2nd	23.492	30.11	9.159	2.288
3rd	18.097	23.20	7.057	2.289
4th	14.763	18.92	5.757	2.28
5th	12.391	15.88	4.832	2.290

Chapter 5

CONCLUSION

In this thesis, the performance of graphitized silicon carbide (EG/SiC) electrode systems, in view of their graphitization induced novel surface and interface properties, for Al-ion battery application has been explored using different techniques. The techniques, cyclic voltammetry and galvanostatic charge-discharge method, helped us to understand important properties of two different electrode systems. First, I have analyzed the bare SiC working electrode and then epitaxially graphene layered SiC electrode by both techniques. If we compare the results of the cyclic voltammetry technique for both electrodes, then we can conclude that EG/SiC working electrode shows comparatively better results. The graphene layers helped in providing more stability to the electrode system. And that's why less irreversible redox reactions occur in the case of EG/SiC WE. Proof of less number of irreversible redox reactions can be seen in the voltammogram of the EG/SiC working electrode. If we compare data from tables 3 and 5, then it is clearly visible that the difference between anodic and cathodic peak values for different CV cycles is less compared to bare SiC WE. And that's why the cyclic efficiency of the EG/SiC working electrode will be high. But still, there is a requirement to improve more its cyclic efficiency. Galvanostatic data analysis of both the electrodes made things more clear as by using this method, we can calculate specific charge capacity and specific energy density of the system. And cyclic efficiency can also be predicted for a large number of charge-discharge cycles. The time taken during discharging cycle is more in the case of the EG/SiC working electrode, and we know that specific charge capacity is directly proportional to the time taken; that's why EG/SiC WE electrode has more charge capacity and also cyclic efficiency than the bare SiC electrode. And other properties like specific capacitance, specific energy density, and power density have also improved after graphene coating. But there are still problems with both electrode systems when we compare them to the other battery systems like Li-ion batteries. So this research field has a very vast area for research to make aluminium ion battery a sustainable battery system. Although research in this field has already started at a good pace, more research is required because it is one of the most sensitive topics of the present time. The thesis work shows that novel aluminium ion batteries require more attention in the research field as they can provide the solution for sustainable energy storage systems and future energy demands

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