THIN FILM COATING AND ITS APPLICATION IN ENERGY STORAGE SYSTEM

M.Sc. Thesis

By **REKHA AGARWAL**



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THIN FILM COATING AND ITS APPLICATION IN ENERGY STOAGE SYSTEM

A THESIS

Submitted in partial fulfilment of the requirements for the award of the degree of Master of Science

> by REKHA AGARWAL



DISCIPLINE OF PHYSICS INDIAN INSTITUTE OF TECHNOLOGY INDORE JUNE 2016

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INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **THIN FILM COATING AND ITS APPLICATION IN ENERGY STORAGE SYSTEMTLE OF M.SC. THESIS** in the partial fulfilment of the requirements for the award of the degree of **MASTER OF SCIENCE** and submitted in the **DISCIPLINE OF PHYSICS, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from July 2014 to June 2016 under the supervision of Dr. Sudeshna Chattopadhyay, Assistant professor, Discipline 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.

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Dedicated to

My country, INDIA

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Abstract

With the constantly increasing worldwide need for energy, fossil-based fuels (coal, petroleum, and natural gas) as our main energy sources are rapidly decreasing, while their combustion is increasing the output of greenhouse gases and other pollutants in our environment. Therefore, there is an urgent need to seek renewable clean energy sources like, solar energy, wind energy etc. as alternatives. Energy storage is a critical issue in supporting the extensive applications of these renewable energy sources. Batteries are used widely to store electrical energy in the form of chemical energy. Currently, Li-ion batteries have been extensively investigated as the principal electrical energy storage (EES) system due to their outstanding energy and power density. But, their main disadvantages include high cost, limited lithium resources in the earth's crust, reliability and safety. Due to the low cost, higher safety, low-flammability, lower reactivity, environmental friendliness and natural abundance of aluminium, the Al-ion battery has displayed excellent prospects. However, there is a requirement for better cathode material for the Al-ion battery system in terms of better capacity, higher safety, lower cost and longer recyclability (or lifetime). Here, we report on a novel Al-ion battery using SiC nanoparticles as the cathode against an aluminum metal anode in an ionic liquid based electrolyte. Silicon carbide (SiC) has been regarded as one of the most promising electrode materials due to its high theoretical capacity, in addition to its non-toxicity, environmental friendliness and low cost. It has been observed that the Al-ion battery (using SiC as cathode) delivered first discharge capacity of 97mAh/g with capacity fading in subsequent cycles. Further, it has been demonstrated that epitaxial graphene on silicon carbide (EG/SiC) delivered first discharge capacity of 121mAh/g. So, with the thin coating of graphene on SiC, the first discharge capacity has been increased significantly (almost 25%).

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ACRONYMS

Al	Aluminium
AIB	Aluminium – ion Batteries
CCSP	Controlled Current Stripping Potentiometry
СР	Chronopotentiometry
EC	Electrochemical Capacitors
EES	Electrical Energy Storage
EG	Epitaxial Graphene
emf	Electro Motive Force
FESEM	Field Emission Scanning Electron Microscopy
НЕРА	High Efficiency Particular Arresting
Li	Lithium
LIB	Lithium – ion Batteries
NaS	Sodium Sulphur
NATO	North Atlantic Treaty Organization
NiCd	Nickel Cadmium
NMP	N-Methyl-2-pyrrolidone
OCP	Open Circuit Potential
PLC	Programmable Logic Controller
PSA	Potentiometric Stripping Analysis
PVDF	Polyvinylidene fluoride
R&D	Research And Development
SEM	Scanning Electron Microscopy
SHE	Standard Hydrogen Electrode
SiC	Silicon Carbide
UPS	Urgent Power Supply
Wh	Watt Hour
XRD	X-Ray Diffraction

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Chapter 1 Introduction

Electrical Energy Storage (EES) refers to a process of converting electrical energy from a power network into a form that can be stored for converting back to electrical energy when needed [1-3]. Electrical energy storage systems can be divided into two main categories: **Batteries and Electrochemical Capacitors (ECs).**

Batteries store energy in the form of chemical reactants, whereas ECs (also called as Supercapacitor, Ultra-capacitor, or Electrochemical double-layer capacitor) store energy directly as charge. Due to this fundamental difference between the systems, they exhibit different energy and power outputs, charge-discharge cycleability, and reaction time scales. Batteries can generally store significantly more energy per unit mass than ECs (fig.1.1) because they use electrochemical reactions called Faradaic processes. Faradaic processes involve the transfer of charge across the interfaces between a battery's electrodes and electrolyte solution, lead to reduction and oxidation, or redox reactions, of species at the interfaces. When a battery is charged or discharged, the redox reactions change the molecular or crystalline structure of the electrode materials, which often affects their stability, so batteries generally must be replaced after several thousand charge-discharge cycles. On the other hand, ECs show no major changes in the properties of the electrode materials during the operation, so they can be charged and discharged up to millions of times. The charge-storing processes employed in ECs are much faster than the Faradaic processes in batteries, so although ECs have lower energy densities than batteries, they have higher power densities (Fig.1.1).





Furthermore, their operation time scales are quite different: ECs can be charged and discharged in seconds, whereas high-performance rechargeable batteries require atleast tens of minutes to charge and hours or days to discharge. These differences have made for different market applications and opportunities, depending on the performance needs. In fact, some important applications require the use of batteries and ECs in combination. For example, the next generation of hybrid vehicles will likely incorporate batteries and ECs.[5]



Fig.1.2 Charging and Discharging of an electric double-layer capacitor

Like a conventional capacitor, an electrochemical capacitor stores energy as charge on a pair of electrodes. Unlike a conventional capacitor, however, an EC stores charge in an electric double layer that forms at the interface between an electrode and an electrolyte solution [6], as shown in fig.1.2.

A brief description about different types of batteries and its components:

Batteries: A battery is composed of an anode (negative electrode), a cathode (positive electrode) and an electrolyte that allows for ionic conductivity. Rigid separators (made of polymeric materials, for example) separate the anode and cathode to prevent the short circuit. In general, battery is made of two electrochemically active couples, the electrodes being separated by an ionically conductive, electronically insulating medium (electrolyte) [4]. Electrons are forced to transfer from one electrode to another through the external circuit while, at the same time, electro neutrality is ensured by ion transport across the electrolyte (fig.1.3).





When one of the redox reactions is finished, the electron flow (current) stops. If the process can be reversed by applying an external current, batteries can be recharged. Rechargeable batteries are also termed secondary batteries, while non-rechargeable batteries are called primary batteries [7].

In rechargeable batteries, there are monovalent, divalent and trivalent type batteries. Most commonly used monovalent batteries include Sodium (Na) ion batteries and Lithium (Li) ion batteries. Divalent batteries and trivalent type batteries include Magnesium ion batteries and Aluminium (Al) ion batteries respectively.

Batteries are in some ways ideally suited for electrical energy storage applications. They not only provide fuel flexibility and environmental benefits, but also offers a number of important operating benefits to the electricity utility. They can respond very rapidly to load changes and accept co-generated and/or third-party power, thus enhancing the system stability. Batteries usually have very low standby losses and can have high energy efficiency (60%-95%). The construction of a secondary battery is facilitated by the short lead times, potentially convenient sitting, and the technology's modularity [8, 9]. However, large scale utility battery storage has been rare up until fairly recently because of low energy densities, small power capacity, high maintenance costs, a short cycle life and a limited discharge capability. In addition, most batteries contain toxic materials and hence the ecological impact from uncontrolled disposal of batteries must always be considered. Batteries that are either in use and/or potentially suitable for utility scale battery energy storage applications include lead acid, nickel cadmium, sodium sulphur, sodium nickel chloride and Li-ion [10].

1. Lead acid batteries

Lead acid batteries, invented in 1859, are the oldest and most widely used rechargeable electrochemical devices. A lead acid battery consists of (in the charged state) electrodes of lead metal and lead oxide in an electrolyte of about 37% (5.99 M) sulphuric acid. In the discharged state both electrodes turn into lead sulphate and the electrolyte loses its dissolved sulphur acid and becomes primarily water. The chemical reactions are as follows:

(i) Anode: $Pb + SO_4^{2-} \leftrightarrow PbSO_4 + 2e^{-1}$

(ii) Cathode: $PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \leftrightarrow PbSO_4 + 2H_2O$

There are several types of lead acid batteries including the flooded battery requiring regular topping up with distilled water, the sealed maintenance free battery having a gelled/ absorbed electrolyte, and the valve regulated battery. Lead acid battery has a low cost (\$300–600/kWh), and a high reliability and efficiency (70%–90%). It is a popular storage choice for power quality, UPS and some spinning reserve applications. Its application for energy management, however, has been very limited due to its short cycle life (500–1000 cycles) and

low energy density (30–50 Wh/kg) due to the inherent high density of lead. Lead acid batteries also have a poor low temperature performance and therefore require a thermal management system. Nevertheless, lead acid batteries have been used in a few commercial and large-scale energy management applications such as the 8.5 MWh/1 h systems in BEWAG Plant (Berlin, Germany), the 4 MWh/1 h systems at the Iberdrola Technology Demonstration Centre (Madrid, Spain), and the 14 MWh/1.5 h systems in PREPA (Puerto Rico). The largest one is a 40 MWh system in Chino, California (USA), which works with a rated power of 10 MW for 4 h [11].

2. Nickel cadmium batteries

Nickel cadmium batteries (NiCd) rank alongside lead acid systems in terms of their maturity and popularity. NiCd batteries contain a nickel hydroxide positive electrode plate, a cadmium hydroxide negative electrode plate, a separator, and an alkaline electrolyte. NiCd batteries usually have a metal case with a sealing plate equipped with a self-sealing safety valve. The positive and negative electrode plates, isolated from each other by the separator, are rolled in a spiral shape inside the case. The chemical reaction is NiCd batteries have a high energy density (50–75 Wh/kg), a robust reliability and very low maintenance requirements, but relatively low cycle life (2000–2500 cycles). These advantages over lead acid batteries make them favoured for power tools, portable devices, emergency lighting, UPS, telecoms and generator starting. However, portable devices such as mobiles, telephones and laptops have effectively been displaced from these markets by other electro chemistries over the past decade.

The main drawback of NiCd batteries is the relatively high cost due to the expensive manufacturing process. Cadmium is a toxic heavy metal hence posing issues associated with the disposal of NiCd batteries. NiCd batteries also suffer from "memory effect", where the batteries will only take full charge after a series of full discharges. Proper battery management procedures can help to mitigate this effect. The NiCd system has also achieved significant prominence in terms of its application in the "world's largest (most powerful) battery", at Golden Valley, Fairbanks, Alaska, USA [12, 13]. It comprises of four battery strings, each of 3440 cells, with a string voltage of 5200 V. The batteries are expected to perform 100 complete and 500 partial discharges in the system's 20-years design life. The system here provides critical spinning reserve functionality in what is effectively an "electrical island".

3. Sodium sulphur

A NaS battery consists of liquid (molten) sulphur at the positive electrode and liquid (molten) sodium at the negative electrode as active materials separated by a solid beta alumina ceramic electrolyte [3]. The electrolyte allows only the positive sodium ions to go through it and combines with sulphur to form sodium polysulphides:

$2Na + 4S \leftrightarrow Na_2S_4$

During discharge positive Na⁺ ions flow through the electrolyte and electrons flow in the external circuit of the battery producing 2.0 V. This process is reversible as charging causes sodium polysulphides to release the positive sodium ions back through the electrolyte to recombine as elemental sodium. The battery is kept at 300–350°C. NaS batteries have a typical cycle life of 2500 cycles. Their typical energy and power density are in the range of 150-240 and 150-230 W/kg, respectively. NaS battery cells are efficient (75%-90%) and have a pulse power capability over six times their continuous rating (for 30 s). This attribute enables NaS batteries to be economically used in combined power quality and peak shaving applications. The NaS battery technology has been demonstrated at over 298 sites in Japan totalling more than 20 MW with stored energy suitable for 8 h daily peak shaving such as the 6 MW/8 h unit in the Tokyo Electric Power Company and the 8 MW/7.25 h at a Hitachi Plant. Such applications of NaS in the U.S. market are under evaluation. American Electric Powers have launched the first demonstration of the NaS system in Ohio with a capacity up to 1.2 MW. The major drawback is that a heat source is required which uses the battery's own stored energy, partially reducing the battery performance, as the NaS battery needs to operate at a high

temperature (300-350°C) as mentioned above. Initial capital cost is another issue, but it is expected to fall as the manufacturing capacity is expanding.

4. Sodium nickel chloride

The sodium nickel chloride battery is better known as the ZEBRA battery [14]. It is a high temperature $(300^{\circ}C)$ system that uses nickel chloride as its positive electrode and has the ability to operate across a broad temperature range (-40°C to +70°C) without cooling. The chemical reaction occurring in a ZEBRA battery is:

Compared to NaS batteries, ZEBRA batteries can withstand limited overcharge and discharge and have potentially better safety characteristics and a high cell voltage (2.58 V). The disadvantages with respect to NaS batteries are their low energy density (120 Wh/kg) and power density (150 W/kg), although the former still represents a considerable improvement over the lead acid battery technology. Another disadvantage is that only one company, the Beta R&D (UK), in the world produces this kind of battery and the technology was acquired by MES (Swiss) in 1999. Beta R&D became an independent company in 2003 following a management buyout. At present Beta R&D is developing a high power version of the ZEBRA battery for hybrid electric vehicles, a high energy version for storing renewable energy and a load-levelling battery for industrial applications. The application of the ZEBRA batteries in the new NATO Submarine Rescue System (NSRS) has also been announced recently.

5. Lithium ion batteries

The cathode in this kind of battery is lithiated metal oxide (LiCoO₂, LiMO₂, LiNiO₂, etc.) and the anode is made of graphite with a layered structure. The electrolyte is made up of Li salts (such as LiPF₆) dissolved in organic carbonates. When the battery is charged, the Liatoms in the cathode become ions and migrate through the electrolyte toward the graphite anode where they combine with external electrons and are deposited between the graphite layers as Li-atoms. This process

is reversed during the discharge process. Li-ion batteries, first proposed in the 1960s, came into reality when Bell Labs developed a workable graphite anode to provide an alternative to Li metal (Lithium battery). The first commercial Li-ion batteries were produced by Sony in 1990. Since then, improved material developments have led to vast improvements in terms of the energy density (increased from 75 to 200 Wh/kg) and cycle life (increased to as high as 10,000 cycles). The efficiency of Li-ion batteries is almost 100% which is another important advantage over other batteries. Although Li-ion batteries take over 50% of the small portable devices market, there are some challenges for making large-scale Li-ion batteries. The main hurdle is the high cost (>\$600/kWh) due to special packaging and internal overcharge protection circuits [3].

Advances in batteries based on the use of alkali metals (Li and sodium) at the negative electrode took place later in time (starting in the 1960s) and, hence, benefited from a larger degree of scientific knowledge at all levels. Their advantage stems from their low atomic weight, which results in high electrochemical capacities: 3860 Ah/kg for Li and 1170 Ah/kg for sodium. Furthermore, due to their high standard reduction potentials, large cell voltages are derived from coupling these electrodes with low standard reduction potential species. Thus, theoretical energy densities are larger than those obtainable with the aforementioned lead/acid- or nickel-based technologies. The prospects of building batteries using alkali metals requires moving away from aqueous media, since they are electrochemically unstable at its potentials of operation. The use of alternative non-aqueous electrolytes adds some complexity to the picture, since electrochemistry in these media is much less well-developed. Additionally, battery fabrication involves constructing the cells in a moisture-free environment. The development of sodium cells has been aimed at achieving high specific energy with readily available non-strategic starting materials. A derivative of this technology, termed the ZEBRA battery, was later evaluated for automotive applications, having the advantage of being assembled in the discharged state and hence avoiding the need to

handle liquid sodium.

Nowadays, due to their outstanding energy and power density, Li-ion batteries have become a mainstay for EES [15-17]. However, the concerns regarding the high cost and the limited Li reserves in the earth's crust have driven the researchers to search more sustainable alternative energy storage solutions [18-20].

Sodium-ion and Magnesium-ion batteries, as new energy storage systems in portable devices, have attracted much attention of the investigators. Most recently, Al-ion battery (AIB) with multivalent metal ions transmitting internally has been studied preliminarily. Owing to its low cost, easy operation and high security, the Al-ion battery exhibits excellent prospects. However, the capacity and the cycle life are not satisfying at present.

Some multivalent metal elements, such as aluminium and titanium, are abundant metallic elements in the earth's crust with low price. Most important of all, comparing to Li-ion and Na-ion batteries with only one charge transferred in one redox couple, batteries with multivalent metal ions running between anodes and cathodes can transfer more charges in one redox couple, indicating a promising energy storage device for large capacity. Herein, we define this kind of battery as super-valent battery.

From the viewpoint of practical application, AIB is more favourable in the aspects of cost, environment and safety when compared with the LIBs. First of all, Al is much cheaper than Li and can be recycled. Considering billions of small LIBs consumed each year in phones and laptops, this AIB technology can be revolutionary if we can further enhance the performance to the same level as LIB. Second, Li is toxic and easy to catch fire, while Al is non-toxic and non-flammable in air due to the existence of a surface passivation layer. Therefore, the use of AIBs would help to eliminate the environment problems caused by disposal of LIBs. Furthermore, unlike the conventional LIBs using highly ignitable organic electrolyte, this new AIB system will not burst into fire because the electrolyte is basically a liquid salt at room temperature with low flammability. Another noteworthy advantage of the new AIBs is its flexibility. As demonstrated in a polymer-coated pouch cell, this AIB system can be potentially shaped or molded with variable sizes to satisfy different applications such as wearable electronics.

Thus, we concluded that Li-ion batteries have been extensively investigated due to their excellent energy and power density. However, their disadvantages are obvious, including cost, lithium resource, reliability, and safety. Owing to the natural abundance and low cost of Al, Al-based batteries have become one of the candidates for energy storage devices. The Al-ion battery system has been investigated for years; however, due to the fast corrosion and hydrogen evolution reaction between Al and the electrolyte, the utilization of the electrode is reduced, even leading to the scrappage of the battery. Recently, an Al-ion battery with multivalent metal ions transmitting internally has attracted much attention, such as VO₂, V₂O₅, anatase TiO₂ in aqueous solution, fluorinated natural graphite, polymers, copper hexacyanoferrate and prussian blue analogues. However, none of them is satisfactory for their low capacity, low voltage plateau or short cycle life. We established a new kind of Al-ion battery with SiC as a cathode material.

CHAPTER 2

2.1 Theoretical background

In a battery system, oxidation reaction takes place at anode whereas reduction reaction at cathode. Open circuit potential (OCP) is the potential in a working electrode comparative to reference electrode when there is no current passing in the cell. It refers to the difference that exists in electrical potential which depends on the cathode, anode and electrolyte.

2.1.1 Faraday laws of electrolysis:

First Law

(1) The amount of chemical change produced by current at an electrode-electrolyte boundary is proportional to the quantity of electricity used.[21, 22]

Second law

(2) The amounts of chemical changes produced by the same quantity of electricity in different substances are proportional to their equivalent weights.[21, 22]

In electrolytic reactions, the equivalent weight of a substance is the gram formula weight associated with a unit gain or loss of electron. The quantity of electricity that will cause a chemical change of one equivalent weight unit has been designated as one faraday which is equivalent to 9.6485309×10^4 Coulombs of electricity.[22]

2.1.2 The effect of temperature on cell potential:

Laws of Thermodynamics

Zeroth Law of Thermodynamics states that if the two systems are in thermal equilibrium with a third systems then they are also in thermal equilibrium with each other.

First Law of Thermodynamics is a statement of the law of conservation of energy which states that energy can neither be created nor destroyed although it can be converted from one form to another. Mathematically, change in internal energy (ΔU) of a close system is due to heat added or removed from the system (Q) and/or work done on or

by the system (W).

$$\Delta \mathbf{U} = \mathbf{Q} + \mathbf{W}$$

Second Law of Thermodynamics states that when energy changes from one form to another form, or matter moves freely, the entropy of the universe tends to increase. Therefore, all spontaneous events are accompanied by an increase in the entropy of the universe. Entropy (S) is a measure of disorder.

Third Law of Thermodynamics states that the entropy of a perfectly crystalline substance at zero K or absolute zero is take to be zero.[23] When these laws are applied to chemical reactions, they relate the equilibrium condition (whether the reaction is proceeding in the forward or reverse direction) and the temperature of the reaction to the thermodynamic functions, namely change in enthalpy (Δ H), change in entropy (Δ S) and change in free energy (Δ G). By studying the effect of temperature on the equilibrium condition for a chemical reaction, we can calculate these thermodynamic functions.[24-27]

By examining ΔH , ΔS and ΔG in a chemical system, a wealth of information may be extracted. In thermodynamics, a system is the particular part of the universe being studied. Enthalpy describes changes of heat in a system. If the system absorbs heat during a given process then the process is said to be endothermic and the change in enthalpy (ΔH) is greater than zero ($\Delta H > 0$). On the contrary, if the system releases heat then the process is called as exothermic and ($\Delta H < 0$).

As mentioned above, entropy is the measure of disorder or randomness in a system. The greater the order in a system, the lower the entropy. The lower the order in a system, the higher the entropy.

The Gibbs Free Energy (G) is the function derived from H and S. The change in free energy (ΔG) is a composite function that gives a measure of the spontaneity of a reaction. If $\Delta G < 0$, a reaction will occur spontaneously. If $\Delta G > 0$, the reaction is non-spontaneous. If $\Delta G = 0$ the system is at equilibrium. The mathematical form for ΔG is the following:

$$\Delta G = \Delta H - T \Delta S$$

Where T is the absolute temperature (in Kelvin). The effect of the sign of Δ H and Δ S and the effect of temperature on spontaneity of a reaction can be summarized as follows[28]:

 Table 2.1: Spontaneity of a reaction

∆H _{system}	∆S _{system}	Process
-	+	Spontaneous at all temperature
+	-	Non-spontaneous at all temperature
+	+	Spontaneous at high temperature
-	-	Spontaneous at low temperature

Thermodynamics and Equilibrium:

For a general reaction or process of reactants A and B giving products C and D:

$$aA + bB \rightarrow cC + dD$$

Then, the reaction quotient, Q, is

$$Q = \frac{[c]^{c}[D]^{d}}{[A]^{a}[B]^{b}}$$

 ΔG of a process at any concentration of A, B, C, and D, is given by the equation:

$$\Delta G = \Delta G^{o} + RT \ln Q$$

Where ΔG^{O} is the free energy of the reaction under the defined standard conditions of 1 atmospheric pressure and 1 M concentrations of reactants. ΔG is the observed change in free energy at conditions other than standard. At equilibrium, $Q = K_{eq}$ and hence reaction favours neither products nor reactants at equilibrium and therefore $\Delta G = 0$. Under these conditions above equation becomes:

$$\Delta G^{o} = -RTlnK_{eq}$$

The cell potential of a redox process is related to the free-energy change as follows:

$$\Delta G^{o} = -nFE^{o}$$

In this equation, F is Faraday's constant, the electrical charge on 1 mole of electron 1F = 96,500 C/mol e⁻ = 96,500 J/V-mol e⁻ and n represents the number of moles of electrons transferred in the reaction. In case, when both reactants and products are in their standard states, above equation can be written as:

$$\Delta G^{o} = -nFE^{o}$$

2.1.3 Mass transport:

The Faradaic current that flows at any time is a direct measure of the rate of the electrochemical reaction taking place at the electrode. Further, the current itself is dependent upon two things: 1) the rate at which material gets from the bulk of solution to the electrode, known as mass transport, and 2) the rate at which electrons can transfer across the interface, or charge transfer kinetics. These two processes are inexorably intertwined in the flow of current.

There are three basic mechanisms of mass transport:

Diffusion: The movement of molecules from a region of high concentration to a region of lower concentration as shown in fig.2.1 for one dimension is called diffusion. The rate at which a molecule diffuses is dependent upon the difference in concentration between two points in solution called as the concentration gradient and on the diffusion coefficient, D, which has a characteristic value for a specific solution species at fixed temperature.



Fig.2.1 Diffusion Process

This movement of a chemical species under the influence of a concentration gradient is described by Fick's first law.[29, 30] A particle i will diffuse through a cross-sectional area as a function of the concentration gradient across the selected area. Flux, as particles per unit time across the given segment, is expressed as J_i according to

$$\mathbf{J}_{i} = - \operatorname{Di} \left(\partial \mathbf{C}_{i} / \partial \mathbf{x} \right)$$

Where, $\partial C_i / \partial x$ expresses the concentration gradient and D_i is the diffusion coefficient for particle i.

Migration: The movement of charged particles in response to a local electric field is called migration. The contribution of migration to the total flux is proportional to the charge of the ion, the ion concentration, the diffusion coefficient and the magnitude of the electric field gradient experienced by the ion.[31] A change in the applied potential to a solid electrode in a solution containing ions affect charge migration as illustrated in fig.2.2 for increasing negative charge at the electrode surface.



Fig.2.2 Migration process of ions

Convection: The movement of fluids is described by hydrodynamics. Convection is defined as forced movement of solution species by mechanical (stirring) or other means. The rate at which a solution is stirred can generally be controlled, with the convective contribution (in one dimension) to total flux of a species described in terms of its hydrodynamic velocity, v_x . [30, 32]The effect of stirring a solution is shown in fig.2.3.



Fig.2.3 Convection process

Total Mass Transport: The total mass transport of material or flux, to an electrode is described for one dimension by the **Nernst-Planck** equation.

 $J(x,t) = - [D(\partial C(x,t) / \partial x)] - [(zF/RT)DC(x,t)](\partial \phi(x,t) / \partial x) + C$ $(x,t) v_x(x,t)$

Where J is the flux (mol cm⁻² s⁻¹), D is the diffusion coefficient of the solution species (cm²/s), C is the concentration of the species (mol/cm³), φ is the electrostatic potential (V) and v_x is the hydrodynamic velocity (cm s⁻¹). The Nernst-Planck equation combines the individual contributions from diffusion (concentration gradient), migration (electric field) and convection (hydrodynamic velocity). This equation shows that the flux of material towards the electrode surface is proportional to either of three slopes of concentration, electrostatic potential or hydrodynamic velocity, all as a function of distance from the electrode surface. Electrochemical experiments can be designed to eliminate the contributions of electrostatic potential and hydrodynamic velocity to the overall flux of electroactive species, limiting mass transport to the contribution from diffusion. The current resulting from

these experiments can then be classified as diffusion controlled. Contributions from migration can be effectively eliminated by adding an inert electrolyte to the solution at a 10 - 100 fold excess with respect to the redox couple of interest. The electric field between the two electrodes involved in the measurement is dissipated over all of the ions in solution and not just the electroactive material. Under these conditions, the contribution of migration to the observed current is <1%. Contributions from convection can be reduced or eliminated by working in quiet (unstirred) solutions. With careful control of external vibration and temperature, diffusion controlled measurements for upto 20 seconds or so can be made without significant convective effects. The flux can then be related to the observed current at the working electrode by

$$i t = n FAD (\partial Ci / \partial x) | x = 0$$

Where A is the electrode area (cm²) and other symbols have explained earlier. [33, 34]

2.1.4 Working principle of battery:

For understanding the basic principle of battery, basic concept of electrolytes and electron affinity should be understood properly. When two dissimilar metals or metallic compounds are immersed in an electrolyte, there will be a potential difference produced between these two. It is found that, when some specific compounds are added to water, they get dissolved and produce negative and positive ions. This type of compound is called an electrolyte. The popular examples of electrolytes are almost all kinds of salts, acids, and bases etc.



Fig.2.4 Charge and discharge mechanism of battery

The energy released during accepting an electron by a neutral atom is known as electron affinity. As the atomic structure for different materials are different, the electron affinity of different materials will differ. If two different kinds of metals or metallic compounds are immersed in the same electrolyte solution, one of them will gain electrons and the other will release electrons. Which metal (or metallic compound) will gain electrons and which will lose them depends upon the electron affinities of these metals or metallic compounds. The metal with low electron affinity will gain electrons from the negative ions of the electrolyte solution. On the other hand, the metal with high electron affinity will release electrons and these electrons come out into the electrolyte solution and are added to the positive ions of the solution. In this way, one of these metals or compounds gains electrons and another one lose electrons. As a result, there will be a difference in electron concentration between these two metals. This difference of electron concentration causes an electrical potential difference to develop between the metals. This emf can be utilized as a source of voltage in any electronics or electrical circuit.

2.1.5 Electrochemical series:

The standard reduction potentials of a large number of electrodes have been measured using standard hydrogen electrode as the reference electrode. These several electrodes can be arranged in the increasing or decreasing order of their reduction potentials. Arrangements of the elements in order of increasing reduction potential values are known as **Electrochemical Series**. It is also known as **activity series** of a few typical electrodes.

Characteristics features of Electrochemical Series

(i) The negative sign of the standard reduction potential indicates that an electrode when joined with standard hydrogen electrode (SHE) acts as anode and oxidation occurs on this electrode. For instance, standard reduction potential of zinc is -0.76 V, when zinc electrode is joined with SHE, it acts as anode (negative electrode) that is oxidation takes place on this electrode. Similarly, the +*ve* sign of standard reduction potential indicates that the electrode when joined with SHE acts as cathode and reduction occurs on this electrode.

(ii) The substances, which are stronger reducing agents than hydrogen are placed above hydrogen in the series and have negative values of standard reduction potentials. All the substances which possess positive values of reduction potentials and placed below hydrogen in the series are weaker reducing agents than hydrogen.

(iii) Substances, which are stronger oxidizing agents than H^+ ion, are placed below hydrogen in the series.

(iv)The metals on top (having high negative value of standard reduction potentials) have the tendency to lose electrons readily. These are usually active metals. The activity of metals decreases from top to bottom. The non-metals on the bottom (having high positive values of standard reduction potentials) have the tendency to accept electrons bottom readily. These are active non-metals. The activity of non-metals increases from top to bottom.



Table: 2.2 Standard reduction electrode potentials at 298K

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2.1.6 Sample Preparation and Characterizing Techniques:

1. Hot Air Oven:-

Working Principle: There is a forced circulation of hot air inside the chamber of oven. When hot air reaches the top of the chamber, it is circulated back to the bottom by a fan installed inside the chamber and hence optimum amount of heat is achieved gradually inside the chamber of hot air oven. We had used hot air over for drying our samples at 50°C to 70°C.



Fig.2.5 Hot Air Oven

2. Argon filled glove box:

A glove box is a hermetically sealed enclosure. It provides a working space in its inner side which completely segregated from the outside environment. Glove box is designed to maintain an artificial atmosphere inside, consisting of pure argon with a concentration of oxygen and water vapour typically below 1 ppm. It is used to prevent the unwanted reaction with oxygen and water vapour.

The glove box system works on the principle of gas circulation: The working gas continuously circulates between the glove box and the gas purifier. The gas purification system removes moisture and oxygen from the inert gas glove box atmosphere. It utilizes a proprietary reactive agent to withdraw oxygen from the inert gas. A proprietary adsorbent removes water. When the gas purification system becomes exhausted, it can be regenerated in a PLC-controlled process by passing a regeneration gas through it.



Fig.2.6 Argon filled glove box

Table 2.3 Function of glove box and its parts

Sr.	Parts	Function
No.		
1	Glove	Hermetically sealed working space
	Box	

2	Window	Central controlling and monitoring the system.
	with	(as part of the gas purifier or attached to the glove
	Glove	box as shown in this picture).
	Ports	Accessing system functions and system
	and	parameters
	Gloves	
3	Control	Central controlling and monitoring the system.
	Panel	(as part of the gas purifier or attached to the glove
		box as shown in this picture).
		Accessing system functions and system parame-
		ters
4	Antecham	Transferring materials into and out of the glove
	ber	box without contaminating the atmosphere inside
		the box.
5	Main	Turning the system on and off
	Switch	
6	Gas	To remove water, oxygen from the inert gas by
	Purificati	continuous circulation over the reactor.
	on System	To remove solvent vapours from the inert gas by
		continuous circulation over solvent removal filter
		(option).
7	Vacuum	To evacuate the antechamber
	Pump	To reduce the box pressure during the regenera-
		tion cycle
8	Flow	Indicates the flow of the regeneration gas during a
	Meter	regeneration cycle.
9	Electrical	Contains electrical and electronic components.
	Cabinet	
10	Easta 't	Turner in and decoursing (1 - 1
10	Footswitc	Increasing and decreasing the box pressure
	h	


Fig.2.7 Circulation process

S.	Parts	Function
No.		
1	Gas flow	Circulation between box and purifier
2	Box	Inlet/outlet of the circulation piping are protected by
	filter	HEPA filters. The filters maintain a particle-free at-
		mosphere and separate the box from the piping and the
		purifier.
3	Valves	Electro-pneumatical valves, PLC controlled.
4	Reactor	Oxygen: Chemical binding by a proprietary reactive
		agent
		Moisture (water vapour): Adsorption on a proprietary
		adsorbent.
5	Blower	Performs the circulation of gas flow; it is encapsulated
	(circulati	in a gas tight enclosure.
	on unit)	
6	Cooling	Electric heat as well as compression heat generated
	(heat	within the gas purifier increases the gas temperature.

exchang	The cooling reduces the temperature of the purified
er)	inert gas before it is directed back to the glove box. A
	convenient, constant temperature inside the glove box
	is maintained.

3. Scanning Electron Microscopy (SEM)

Scanning Electron Microscope is a type of electron microscope that produces image of a sample by scanning it with a focused beam of electrons. The electrons then interact with atoms in the sample producing various signals that can be detected and contains information about the surface topography and composition. In SEM, the electron beam is generally scanned in a raster scan pattern and the beams position is combined with the detected signal to generate an image.

Electrons are generated at the top of the microscope by a metallic filament (A). This region is referred to as the electron gun. The filament is very similar to what you see inside a light bulb. The emitted electrons are then formed into a beam (B) and accelerated down the column toward the specimen. The beam is further focused and directed by electromagnetic lenses (C-E) as it moves down the column. When the beam reaches the specimen, electrons are knocked loose from the surface of the specimen. These electrons are referred to as secondary electrons.



Fig.2.8. Scanning Electron Microscopy

The electron beam scans back and forth across the sample building up an image from the number of electrons emitted from each spot on the sample. This entire process takes place inside a vacuum. The vacuum ensures that the electron beam interacts with the sample rather than the air. Samples to be viewed with the SEM must be able to withstand a vacuum and need to be conductive. Samples that are not conductive can be coated with a thin layer of conductive material by a process called sputter coating.

EDS:

An EDS system typically consists of several key units Fig. 2.9. These include: a semiconductor detector housed with a field-effect transistor (FET) preamplifier, cooled to a sub-ambient temperature; and a main amplifier that provides further amplification. All of this can be fully controlled with a computer-assisted system, such as a multichannel analyzer (MCA) or a computer-assisted X-ray analyzer (CXA), allowing for unattended and automated operation.



Fig.2.9. Energy Dispersive Spectroscopy

When the electron beam hits the sample, there is a high probability that an X-ray will be generated. The resulting X-ray escapes the sample and hits the detector which creates a charge pulse in the detector. This shortlived current is then converted into a voltage pulse with an amplitude reflecting the energy of the detected X-ray. Energy Dispersive Spectroscopy Finally, this voltage pulse is converted to a digital signal and one more count is added to the corresponding energy channel. Once the measurement is completed, the accumulated counts produce a typical X-ray spectrum with the major peaks superimposed on the background. High-energy electrons can interact with atoms in a sample in many different ways, including stimulating the emission of X-rays. In this case, when an electron (from the beam) strikes an atom, it ejects an electron originally positioned in an inner shell (K shell). To return the atom to its lowest energy state, this 'vacancy' is immediately filled by an electron moving from a higher-energy shell in the atom. In doing so, this high-energy electron must release some of its energy in the form of X-rays. As a consequence, the energy released (expressed in eV) is exactly equal to the energy difference between the two levels. All elements except hydrogen and helium produce characteristic Xrays. In addition, practical restrictions concerning a minimum energy level usually exclude the measurement of lithium (0.052 keV), but all other elements, beginning with the beryllium K-shell (0.108 keV), can be assessed simultaneously. X-rays in the range of 100 eV to 20 keV are readily measured with a Si(Li) or SDD detector, and this range can be extended to 100 keV with an HpGe detector. It is this 'energy dispersive' approach that provides the great practical value of EDS, as it enables access to virtually the entire periodic table (except H, He and Li).

4. X-Ray Diffraction (XRD)

XRD is one of the most useful and powerful tools for determining structure of the materials. Along with the determination of the structures, XRD is also used for chemical analysis, stress measurement, phase equilibrium, particle size measurement, etc. The working principle of XRD is based on the scattering of X-rays by the sample. Bragg's law gives the condition for obtaining XRD from a crystalline material.

Bragg's law: $2d \sin\theta = n\lambda$

where, n is the order of diffraction, λ is the wavelength of the characteristic line X-rays, d is inter-planar distance, θ is the angle between the incident collimated X-ray beam and an atomic lattice plane in the crystal.[35]

A powder X-ray diffractometer consists of an X-ray source (usually an X-ray tube), a sample stage, a detector and a way to vary angle θ . The X-ray is focused on the sample at some angle θ , while the detector opposite the source reads the intensity of the X-ray it receives at 2θ away from the source path. The incident angle is than increased over time while the detector angle always remains 2θ above the source path [36, 37]. Sources of X-rays generation are radioisotopes and secondary fluorescence exist, the most common source of X-rays is copper and molybdenum. The tube is evacuated and contains a copper block with a metal target anode and a tungsten filament cathode with a high voltage between them. The filament is heated by a separate circuit, and the large potential difference between the cathode and anode fires electrons at the metal target. The accelerated electrons knock core electrons out of the metal, and electrons in the outer orbitals drop down to fill the vacancies, emitting X-rays. The X-rays exit the tube through a beryllium window. Due to massive amounts of heat being produced in this process, the copper block must usually be water cooled.[38, 39]



Fig.2.10 X-ray Diffractometer

5. Raman Spectroscopy

Raman spectroscopy is a spectroscopic technique based on inelastic scattering of monochromatic light, usually from a laser source. Inelastic scattering means that the frequency of photons in monochromatic light changes upon interaction with a sample. Photons of the laser light are absorbed by the sample and then reemitted. Frequency of the reemitted photons is shifted up or down in comparison with original monochromatic frequency, which is called the Raman Effect. This shift provides information about vibrational, rotational and other low frequency transitions in molecules. Raman spectroscopy can be used to study solid, liquid and gaseous samples.



Fig.2.11 Raman transitional schemes

i) A molecule with no Raman-active modes absorbs a photon with the frequency v_0 . The excited molecule returns back to the same basic vibrational state and emits light with the same frequency v_0 as an excitation source. This type if interaction is called an elastic Rayleigh scattering.

ii) A photon with frequency v_0 is absorbed by Raman-active molecule which at the time of interaction is in the basic vibrational state. Part of the photon's energy is transferred to the Raman-active mode with frequency v_m and the resulting frequency of scattered light is reduced to $v_0 - v_m$. This Raman frequency is called Stokes frequency, or just "Stokes".

iii) A photon with frequency v_0 is absorbed by a Raman-active molecule, which, at the time of interaction, is already in the excited vibrational state. Excessive energy of excited Raman active mode is released, molecule returns to the basic vibrational state and the resulting frequency of scattered light goes up to $v_0 + v_m$. This Raman frequency is called Anti-Stokes frequency, or just "Anti-Stokes".

A Raman system typically consists of four major components: (a) Excitation source (Laser), (b) Sample illumination system and light collection optics, (c) Wavelength selector (Filter or Spectrophotometer) and (d) Detector (Photodiode array, CCD or PMT). A sample is normally illuminated with a laser beam in the ultraviolet (UV), visible (Vis) or near infrared (NIR) range. Scattered light is collected with a lens and is sent through interference filter or spectrophotometer to obtain Raman spectrum of a sample.[40-43]

6. Electrochemical analyser:

Electrochemical workstations comprises of two main components: Electrochemical analyzer and a computer. There exists several techniques like cyclic voltammetry, chronopotentiometry, chronoamperometry, electrochemical impedance spectroscopy, etc. The prepared coin cells are characterized by using electrochemical techniques

(i) Cyclic Voltammetry and (ii) Charge-Discharge methods

6.1 Cyclic Voltammetry:

6.1.1 Electrode Reactions and Electrode Capacitance:

Figure 2.12 describes the process that occurs in simple electrode reactions. In the case of reduction, a species (O) capable of receiving an electron from the electrode diffuses to the surface, receives an electron and diffuses away from the surface. Current at the surface is generated by the transfer of electrons from the electrode to the redox species. In solution current is carried by migration of ions as shown in fig.2.11.



Fig.2.12 Electrode reactions

One can ask whether a current can occur if there is no species in the solution that can transfer electrons to the surface at the potential of interest. The answer is that a transient current can flow because the electrode-solution interface will behave as a capacitor. As the potential of the electrode is varied, ions move to the surface to form a double-layer as shown in fig. 2.12. Although strictly speaking an electrode-solution interface in the absence of a redox couple is not a pure parallel-plate capacitor, it behaves rather like one and a parallel-plate capacitor model is often adequate to describe electrochemical systems. Use of this model allows us to learn about the behaviour of electrodes in the absence of a redox couple. For a simple parallel plate capacitor, charge on the capacitor, Q, is proportional to the voltage drop across

the capacitor, E: Q = CE

The proportionality constant C is the capacitance of the medium. The simplest description of Electrochemical capacitance is the Helmholtz model given by:

$$C /A = \epsilon \epsilon_0 / l$$

where ε is the dielectric constant of the material separating the parallel plates, ε_0 is the permittivity of free space, 1 is the separation between the plates, and A is the area of the electrode. This model does not adequately describe all electrochemical interfaces as the capacitance can depend on both potential and the supporting electrolyte. Still it is a helpful construct. Capacitance is a crucial factor in electrochemical experiments because it gives rise to current during the charging of the capacitor. To calculate the magnitude of this current, we differentiate equation (Q = CE) with respect to t and assume that capacitance is constant:

dQ/dt=C dE/dt

Recognizing that dQ/dt is an expression for current and dE/dt is the potential scan rate v, we obtain:

$$i = Cv$$

From this very simple derivation, an expression for the charging current at steady state when applying a ramping voltage. Thus by measuring the charging current at a given scan rate, one can determine the capacitance of the system. If there is no possibility for electron transfer between the solution and the electrode this is the only current that we will observe.

A simple cyclic voltammetry (no active redox couple present) experiment shown in fig.2.13. On applying the potential form shown in the fig.2.13. initially, a sharp rise in current was observed because of a sharp change in the scan rate v. The current then reaches steady state on

constantly varying the voltage. At reversal of the scan rate, the current changes sign and when on stop scanning, current goes to zero.



Fig.2.13. Schematic explanation of a cyclic voltammetry experiment in the absence of a redox couple

6.1.2 Cyclic Voltammetry with an Active Redox Couple:

The real power of this technique lies in its ability to investigate mechanisms and potentials of electrode reactions. Faradaic current depends on two things: the kinetics of electron transfer and the rate at which the redox species diffuses to the surface. For the redox couple $Fe(CN)_6^{3-/4-}$, the kinetics of electron transfer are reasonably fast, so it was assume at least for the moment that at the surface, the concentrations of $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ can be described by the Nernst equation:

$$E = E^{0'} - 0.0592 \log \left(\frac{[Fe(CN)_6^{-4}]}{[Fe(CN)_6^{-3}]} \right)$$

Where E is the applied potential and E' is the formal electrode potential. As the applied potential becomes more negative, the concentration of $\text{Fe}(\text{CN})_6^{3-}$ must decrease at the electrode surface. It is being reduced to $\text{Fe}(\text{CN})_6^{4-}$. Even with the assumption of Nernstian behaviour, faithful reproduction of the $\text{Fe}(\text{CN})_6^{3-/4-}$ Voltammogram requires an analytical solution to two differential equations.[36]

Qualitative Explanation:

If we assume that concentrations at the surface are governed by the Nernst equation, the concentration of the oxidized species at the surface will decrease as the potential becomes more negative. Assuming that the electron transfer rate is very rapid, the current i that is measured as the potential is decreased will be directly related to diffusion rate of oxidized species to the electrode surface:

i = nFAJ

where n is the number of electrons, F is Faraday's constant, A is the area of the electrode surface and J is the flux of the oxidized species to that surface. The flux is governed by Fick's law:

$$J = -D\left(\frac{dC}{dx}\right)_{x=0} \cong D\frac{(C^* - C_{x=0})}{\Delta x}$$

where, D is the diffusion coefficient of the species, x is the distance from the electrode surface, $(dC/dx)_{x=0}$ is the concentration gradient at the surface, C* is the concentration of the oxidized species in the bulk solution, and $C_{x=0}$ is its concentration at the surface. As you can see, the greater the concentration gradient, the greater the flux J and therefore by equation the greater the cathodic current. The change in the concentration gradient for the cathodic portion of the Cyclic Voltammogram is shown in fig.2.13. Before a potential is applied to the electrode (t=0), there is no concentration gradient, and the solution has the uniform bulk concentration C*. As the potential is applied, the concentration of the oxidized species is depleted at the surface. This lower concentration at the surface gives a higher concentration gradient (at least initially) so according to Fick's law of diffusion equation, we will have more flux to the surface and hence a higher cathodic current. As we continue to make the potential distance from electrode more negative, the concentration of the oxidized species at the surface will eventually go to zero. Simultaneously, the volume in the solution that is depleted of the oxidized species will increase and the concentration gradient will begin to decrease. As the concentration gradient decreases, we will have less flux to the surface and current will begin to decrease. All of this will result in a current-voltage curve that looks like the forward scan in fig.2.13.

As the voltage scan was reversed, depleted layer of the oxidized species was observed, but the surface concentration begins to rise so current decreases further. Finally, a region was achieved where anodic current begins to dominate. Similar concentration profiles were followed for the reduced species where a peak negative current was achieved and then the current was decrease in magnitude as the depletion layer for the reduced species increases.[44, 45]

Quantitative Explanation:

The quantitative simulations show several things for a Nernstian system. The peak current in a Cyclic Voltammogram containing only one species at 25°C is described by:

$$i_p = (2.69 \times 10^5) n^{3/2} . AD^{1/2} . v^{1/2} . C *$$



Fig. 2.14 Shape of a Cyclic Voltammogram for a Nernstian electrochemical reaction

where i_p is the peak current, n is the number of electrons transferred, A is the electrode area, D is the diffusion coefficient of the species, v is the scan rate and C* is the bulk concentration of the species. The difference between E_p and the point where current is half that at E_p , $E_{p/2}$ is (56.5/n) mV at 25°C, where n is the number of electrons transferred. Note that for a Nernstian system, E_p should be independent of scan rate, but i_p will depend on the square root of scan rate. Another useful piece of information is that the separation of anodic and cathodic peaks is about (59/n) mV at 25°C. It is very difficult to achieve a (59/n) mV splitting at most solid electrodes. (If you can achieve 70 mV, you will be doing well. This is a function of electrode preparation as well as scan rate.) If the diffusion constants for the oxidized and reduced species are similar, the value of $E^{o'}$ can be estimated from the average of E pa and E_{pc} , where E_{pa} is the potential of the anodic peak current

and E_{pc} is the potential of the cathodic current. Thus, in your experiments you will use CV to estimate the value of $E^{o'}$ for the $Fe(CN)_6^{3-/4-}$ couple. You will also use the peak current to estimate the diffusion coefficient for $Fe(CN)_6^{3-}$. One other characteristic of a reversible system is that i_{pa} and i_{pc} are the same, but i_{pc} has to be determined as shown in fig.2.13.

6.1.3 Study of Reactions Mechanisms Using Cyclic Voltammetry

The last aspect of CV that we will discuss is its ability to provide information about the chemistry of redox couples. This is perhaps the most attractive feature of this technique.



Fig. 2.15 Cyclic voltammogram of a system where the reduced species is unstable

For example, if a redox couple undergoes two sequential electrontransfer reactions, you will see two peaks in the Voltammogram. If either the reduced or oxidized species is unstable, you might see a Voltammogram such as that shown in fig.2.14. Such qualitative information is very useful.

7. Galvanostatic charge and discharge

The galvanostat uses a three electrode configuration, in which a current is applied between the auxiliary and working electrodes and the potential of the working electrode (measured with respect to the reference electrode) is monitored. The basis of controlled current experiments is that a redox (electron transfer) reaction must occur at the surface of the working electrode in order to support the applied current. Common applications of the galvanostat include constant current stripping potentiometry and constant current electrolysis (including applications where a constant rate of electrolysis is important, such as electrodeposition and battery studies). One advantage of all constant current techniques is that the ohmic drop due to solution resistance is also constant, as it is equal to the product of the current and the solution resistance. The ohmic distortion can therefore be simply corrected by constant potential offset. In contrast, in potentiostatic experiments (e.g. Cyclic voltammetry), the current, and hence the ohmic drop, varies with potential, and correction is more complicated.



Fig. 2.16. (A) Current excitation and potential response (B) For CP (C) Concentration-distance profiles during the reduction of O to R by a current step

Chronopotentiometry (CP) is the most basic constant current experiment. In CP, a current step is applied across an electrochemical cell (without stirring). The current excitation signal and potential response are shown as a function of time in fig.2.16. The nature of the potential response can be rationalized by considering the concentration profiles of the redox species as a function of time. Let us consider the electron transfer reaction O + e = R. Before the current step, the concentration of O at the electrode surface is the same as in the bulk solution (e.g., 5 mM) (fig.2.16 (C)). The initial potential is the rest potential or the open circuit potential ($E_{o.c.}$). Once the (reducing) current step has been applied, O is reduced to R at the electrode surface in order to support the applied current, and the concentration of O at the electrode surface therefore decreases. This sets up a concentration

gradient for O between the bulk solution and the electrode surface, and molecules of O diffuse down this concentration gradient to the electrode surface. The potential is close to the redox potential for O + e = R, and its precise value depends upon the Nernst equation:

$$\mathbf{E} = \mathbf{E}^{\mathbf{O}'} + \frac{0.059}{n} \log \frac{\mathbf{C}_{\mathbf{O}}^{\mathrm{s}}}{\mathbf{C}_{\mathrm{R}}^{\mathrm{s}}}$$

where C_0 and C_R are the surface concentrations of O and R, respectively. These concentrations vary with time, so the potential also varies with time, which is reflected in the slope of the potential vs. time plot at this stage. Once the concentration of O at the electrode surface is zero, the applied current can no longer be supported by this electron transfer reaction, so the potential changes to the redox potential of another electron transfer reaction. If no other analyte has been added to the solution, the second electron transfer reaction will involve reduction of the electrolyte; that is, there is a large change in the potential. The time required for the concentration of O at the electrode surface to reach zero is characterized by time τ . The magnitude of τ depends upon the applied current; for example, an increase in the applied current i leads to a decrease in τ . The quantitative relationship between i and t is defined by the Sand equation:

$$i\tau^{1/2} = \frac{nFAC\pi^{1/2}D^{1/2}}{2}$$

Where, A is the electrode surface area, C is the bulk concentration of the analyte and D is its diffusion coefficient. The parameter $i\tau$ is a useful diagnostic parameter for CP, as it is constant for redox processes that are not complicated by coupled chemical reactions or adsorption. One ubiquitous parameter that causes deviations from the ideal behaviour represented by the Sand equation is the charging current. Charging current is related to changes in potential, and hence is present throughout all constant current experiments. In addition, since the charging current depends upon the rate of change of potential, the magnitude of the charging current (and hence the fraction of the applied current that is available for the faradaic processes) varies during the experiment.

One advantage of CP is that the Sand equation is appropriate for both planar and spherical electrodes; that is, τ is independent of the form of diffusion to the electrode surface.

This should be contrasted with the Cottrell equation, which represents the diffusion-controlled current for a planar electrode at a constant potential. Changing the diffusion from planar to spherical requires a correction term proportional to 1/r to be added to the Cottrell equation. Therefore, the diffusion-controlled current can be complicated if the experiment is run under conditions in which both spherical and planar diffusion are significant (e.g., long time and/or small electrodes).

The Sand equation and the Cottrell equation are also related in that they have been used to calculate diffusion coefficients. However, in the Sand equation, the measured parameter (τ) varies linearly with D, whereas the measured parameter (i) for the Cottrell equation varies with the D^{1/2}. Therefore, better precision can be achieved by using CP and the Sand equation.

It is possible to apply more than one current step in a given experiment. Two-step experiments can be useful in characterizing electrode reactions in which the electron transfer reaction is followed by a chemical reaction. Multiple current step experiments are widely used for charging/discharging study of batteries and other energy sources. A related technique is the measurement of the open-circuit potential as a function of time (this can be considered as equivalent to a CP measurement with an applied current of zero). This is widely used for the study of corroding systems and for potentiometric stripping analysis.[43, 46-49]

7.1 Constant Current Stripping Potentiometry and Potentiometric Stripping Analysis:

These stripping experiments can be used as alternatives to stripping Voltammetric techniques for trace analysis (i.e., measurement of ppb concentrations of e.g., metal ions, DNA). As with stripping Voltammetric experiments, the first stage involves deposition or preconcentration of metal ions from the solution onto the electrode surface. Once this step has been completed, the metal ions are oxidized (stripped) from the electrode surface either by the addition of a chemical oxidizing agent (potentiometric stripping analysis, PSA) or the application of an oxidizing current (constant current stripping potentiometry, CCSP). The potential is monitored as a function of time. It should be noted that the potential response consists of a series of potential steps, which must be further processed in order to generate the more commonly displayed peak-shaped response. A typical potential response is shown in fig.2.17.



Fig.2.17. Typical potential response for a PSA or CCSP experiment 7.2 Characterization of Electrode Reactions Using

Chronopotentiometry:

The characterization of electrode reactions using Chronopotentiometry involves the study of the variation of i $\tau^{1/2}$ with i (fig.2.18). If there are no coupled chemical reactions, i $\tau^{1/2}$ does not vary with i (fig.2.18 a). However, for some electrode reactions that involve coupled chemical reactions (e.g., CE and catalytic reactions), i $\tau^{1/2}$ varies with i in a characteristic manner (fig.2.18 b and c).



Fig 2.18. Variation of $i\tau$ with i for various reactions

For example, $i\tau^{1/2}$ for a CE reaction depends upon the relative values of i and the rate of the chemical reaction, k. If i is large enough, the chemical reaction cannot have any effect and Constant current electrolysis is based on Faraday's law, which relates the total charge passed in an experiment (Q) to the number of molecules electrolyzed (N) and the number of electrons involved in the electron transfer reaction (n): $i\tau^{1/2}$ is determined by the equilibrium concentration of O. If i is decreased to a value at which the chemical reaction can have an effect, then $i\tau^{1/2}$ will increase (since O is generated by the chemical reaction), and will continue to increase as i decreases. The value of i at which the chemical reaction will start to have an effect depends on the magnitude of k; for example, it is smaller for smaller k. The zero current limit of $i\tau^{1/2}$ is related to the sum of concentrations of O and X, since all X is converted to O. The slope of the $i\tau^{1/2}$ vs. Current plot at low i is related to k. The potential responses for reactions that involve adsorption of material to the electrode surface depend upon whether or not the adsorbed

Q = nFN

Where, F is Faraday's constant. The applications of constant current electrolysis can be analytical (measurement of n) or synthetic. Common synthetic applications include the growth of conducting polymers on electrode surfaces or Coulometric titrations (e.g., for the Karl-Fischer determination of water), which involves the in situ generation of the titrant by electrolysis. Other applications include the electrodeposition of metals and battery/fuel cell studies (e.g., charging and discharging at constant current).

8. Ultrasonicater

Sonication is the act of applying sound energy to agitate particles in a sample, for various purposes. Ultrasonic frequencies (>20 kHz) are usually used, leading to the process also being known as ultrasonication.

9. Magnetic stirrer:

A magnetic stirrer is a laboratory device consisting of either a rotating magnet or stationary electromagnets creating a rotating magnetic field. This device is used to cause a stir bar immersed in a liquid to spin very quickly, agitating or mixing the liquid. A magnetic stirrer often includes a provision for heating the liquid. Stirrer are often used in laboratory. In our stirrer we can set its speed from 50 rpm to 1500 rpm. Magnetic stirrers minimize the risks of contamination since only an inert magnet bar, which can easily be cleaned, is put inside the sample/fluid. In addition, using a magnetic stirrer rather than manual stirring is critical for consistent, reproducible mixing or mixing over long time scales



Fig.2.19 Magnetic stirrer

2.2 Review of Past Work and Problem Formulation:

During 1990s, researchers were trying to make Al-ion batteries but they had faced failure due to lack of appropriate electrolytes. With the advent of suitable electrolyte in 2011, several research groups have shown their interest in the fabrication of Al-ion batteries. In 2011, N. Jayaprakash *et al.*, introduced a rechargeable Al-ion battery using V₂O₅ as a cathode, Al as an anode and AlCl₃ in [EMIm]Cl as the electrolyte. For the first time, they had reported the discharge capacity of ~305 mAh/g which remains 273 mAh/g after 20 cycles [50]. Further, in 2012, S. Liu *et al.*, used TiO₂ nanotubes as a potential cathode material for Al-ion battery. The electrochemical Al storage of anatase TiO₂ nanotube arrays in AlCl₃ aqueous solution was investigated. It is firstly demonstrated that Al-ions can be reversibly inserted/extracted into/from anatase TiO₂ nanotube arrays in AlCl₃ aqueous solution due to the small radius steric effect of Al-ions. The maximum discharge capacity of 75 mAh/g is obtained [51]. In 2013, another research group used fluorinated natural graphite as cathode and Al as anode in an ionic (1,3-di-n-butylimidazolium Bromide [bim] liquid [Br]) based electrolyte and this battery showed stable electrochemical behaviour with a discharge capacity of 225mAh/g [52]. In the same year, W. Wang et al., developed Al-ion battery using VO₂ as cathode and aluminium chloride in 1-butyl-3-methyl imidazolium chloride at a molar ratio of 1:1 as electrolyte. The cell delivered a discharge capacity of 165 mAh/g in the initial cycle and 116 mAh/g after 100 cycles [53]. Recently in 2015, H. Sun et al., reported an Al-ion battery using Al-foil as anode, carbon paper as cathode and aluminium chloride as a salt and 1-ethyl-3methyl imidazolium chloride as a solvent with a molar ratio of 1.3:1. At the current density of 50 mA/g, the discharge capacity is 84.55 mAh/g over 50 cycles. Even at a high current density of 150 mA/g , the discharge capacity still remains 62.71 mAh/g over 50 cycles [54]. S. Liu. et al., in 2015, developed an Al-ion battery with copper hexacyanoferrate in acidic aqueous Al₂(SO₄)₃ solution. A specific capacity of 62.9 mAh/g obtained at the current density of 50 mA/g [55]. In 2015, M-C. Lin et al., proposed an Al-ion battery using Al as anode and graphite foam as cathode material using a non-flammable ionic liquid electrolyte (aluminium chloride in 1-ethyl-3-methyl imidazolium chloride at a molar ratio of 1.3:1). The cell exhibited welldefined discharge voltage plateaus near 2 volts, a specific capacity of about 70 mAh/g and a coulombic efficiency of approximately 98%. The cathode was found to enable fast anion diffusion and intercalation, affording charging times of around one minute with a current density of 4,000 mA/g (equivalent to 3,000 W/kg), and to withstand more than 7,500 cycles without capacity decay [56].

Based on literature survey, because of their toxic property, VO_2 and V_2O_5 may not be considered as the good cathode materials although

they have good capacity. Also, the capacity of other cathode materials like carbon paper, graphite foam, copper hexacyanoferrate nanoparticles found to be less efficient for practical applications. In the present scenario, researchers are looking forward for a novel cathode material with appropriate electrolyte combination.

CHAPTER 3

Experimental Details

3.1 SiC as a cathode material in Al-ion batteries

An important argument for the use of graphite as anode material is based on the relatively low volume expansion that occurs upon the intercalation of lithium into the host when the battery is being charged. A disadvantage of graphite, however, is the relatively low electrochemical charge capacity theoretical value 372 mAh/g, which is only about one-tenth of the charge capacity that could theoretically be reached with lithium metal 4235 mAh/g. Therefore, for many years, research has been conducted to find alternative negative electrode materials. However, volume expansion is one of the major issue which occurs upon the insertion/deinsertion of the lithium ions into and from the host material. Much research has been conducted on silicon, as the anode material in Li-ion battery [57-59]. It shows a very high theoretical lithiation capacity. But as in the case of silicon the insertion of lithium is accompanied by a huge volume change of 323%, which leads to a strong mechanical stress of the crystallites and thus to breaking and amorphization of the particles and loss of the electrical contact [60-63]. So in Al-ion battery, we choose SiC as electrode material so that volume expansion can be optimized compared to silicon and capacity is higher than that of graphite.

In First step the structure/ morphology of as received or untreated SiC particles/powder has been characterized.

Fig.3.1(A) shows the X-ray diffraction pattern of the as-received SiC particles. All diffraction peaks of the as-prepared powder can be indexed to the monoclinic crystal structure of SiC (B) phase. The absence of any undesirable peaks demonstrates the presence of a phase pure product and the miller indices (hkl) of all the characteristic peaks are marked as per the standard pattern. The morphology and microstructure are obtained by FESEM images displayed in Figure 3.1(B). The average particle size of as-received SiC particles is ~ 75 nm.





(B)

Fig. 3.1 (A) XRD (B) SEM of bare SiC material

3.2 Steps for coin cell preparation:

Binder preparation: PVDF is most commonly used binder because it is chemically inert and does not react with the electrolyte and Al anode. For binder preparation, we had added PVDF (Polyvinylidene fluoride) in NMP (N-Methyl-2-pyrrolidone) solvent. Ultra-sonication was done for mixing of PVDF in NMP for three hours. During ultra-sonication, the temperature was maintained less than 40°C to protect the damage of binder mixture due to generation of heat during the ultra-sonication process.

Electrolyte preparation: Because of the hygroscopic nature of the AlCl₃, electrolyte preparation has been done inside the glove box where the oxygen and water vapour level is less than 0.5 ppm. The ratio of salt (AlCl₃) to 1-ethyl-3-methyl-imidazolium chloride ([EmIm]Cl) solvent was taken 1.3 : 1. [EmIm]Cl [64, 65] is used as solvent. We mix slowly AlCl₃ into [EmIm]Cl because this process is exothermic. Both salt and solvent is in solid form but after mixing due to exothermic process and low melting points they show a phase change and convert in liquid phase and for proper mixing we used magnetic stirrer for 30 minutes. The as-prepared electrolyte is kept inside the glove box [64, 66-68].

Cathode material preparation: For our cathode electrode we use SiC as the active material. We prepared slurry using active material, conductive carbon and binder at a weight ratio of 60:10:30. Conductive carbon is used for improving the conductivity of cathode material. For uniform mixing of this slurry, we mix it using magnetic bar stirring. We use 50 rpm for half hour and next half hour for 100 rpm for our sample. After this we coat it onto the stainless steel (used as current collector). We dry this slurry using hot air oven for three hours at a temperature of 50-60°C.

Coin cell assembly: Inside the glove box we assembled our 2032 type coin cells. First we insert all the components (separator, cathode, anode and tweezers) inside the glove box. Using coin cell assembling machine, we assembled coin cell. We use electrolyte between the anode and cathode. And spacer and spring for tight binding of coin cell. While preparing the coin cells, the water and oxygen level is maintained less than 1 ppm. After coin cell assembly we removed the cell through antechamber in the glove box.

Coin cell testing: We used electrochemical analyser for coin cell testing. There are four connections: green wire is connected to positive case of coin cell and both white and red wires are connected with

negative case of coin cell and black wire is used for grounding. The results have been discussed in next chapters.

Pressure		
» ⊪	∏ ∢	Cell cap
	«	Spring
	₹	Spacers
8 	∢	Anode
3 	<	Separators
	∢	Cathode
L		Cell cup

Coin cell assembly steps

CHAPTER 4

Results and Discussion

4.1 SIC CATHODE- without any annealing treatment:

Fig.4.1 (A) represents the initial charge/discharge curves of the Al-ion battery using SiC as the cathode at the current density of 4.70mAg⁻¹. The cut-off voltage was set in the range of 0.02–0.8 V.

Chronopotentiometry of bare SiC electrode at 4.70mAg-¹ current density:

Weight of bare SiC electrode = 0.29587 g

Weight of steel spacer = 0.28701 g

Weight of active material = 0.005316 g

Current density = 4.70mAg^{-1} (current = 25μ A)

C rate = 0.048 C





From Fig 4.1 (A) we can calculate the initial cycle discharge capacity is 97mAh/g at current density of 4.7mA/g which is higher than earlier reported cathode materials discharge capacity.





And from Fig. 4.1(B) we see that the first columbic efficiency is 7% which indicates highly irreversible process and less deintercalation process result capacity fading in subsequent cycles columbic efficiency increased to 57% so in further cycles, process tends to reversibility. The first columbic efficiency is less which is mainly due to SEI formation, aggregation of particles, cracking and crumbling of the particles, less active surface area and less active Al-ions.

Cycle	Discharg	Discharg	Charg	Charge	Coulombic
Numbe	e time	e	e time	Capacity	Efficiency
r	(sec)	Capacity	(sec)	(mAh/g)	
		(mAh/g)			
1	74249	96.9943	5244	6.8505	7.06
2	14900	19.4647	4476	5.8477	30.04
3	10807	14.1208	4092	5.3465	37.86
4	7865	10.2753	3325	4.3440	42.27
5	6394	8.3539	3709	4.8452	57.99

Table 4.1 capacity of bare SiC electrode at 4.7mA/g current density

Where Coulombic efficiency = (Charge capacity / Discharge capacity) *100

Cyclic Voltagramme and Chronopotentiometry curve of bare SiC electrode:

Two cathodic and one anodic peaks were observed for the first cycle of Al-ion battery with SiC cathode and AlCl₃ in the [EMIm]Cl electrolyte under the potential window of 0.8 V–0.02 V at the 0.2mV/sec scan rate.. One irreversible peak observed in the first cycle due to SEI formation from Fig. 4.2(A). Because of this irreversible charge transfer our first charging capacity is less compared to first discharging capacity causes low coulombic efficiency.



Fig. 4.2 (A) Cyclic Voltagramme of bare SiC electrode at 0.2 mV/sec scan rate



Fig. 4.2 (B) First cycle Chronopotentiometry curve of bare SiC electrode at 4.7mA/g current density

The first cycle CV peaks well fitted with CP peaks which are shown in table 4.2 indicates stable process in aluminium ion battery.

Table 4.2 Comparison of CV and CP data of bare SiC electrode atfirst cycle

	Cathodic peak	Cathodic peak	Anodic Peak
CV Peaks	0.13v-0.39v	0.52v-0.83v	0.51v-0.64v
CP Peaks	0.48v-0.14v	0.80v-0.54v	0.59v-0.69v
	Peak match cv with cp	Peak match cv with cp	Peak match cv with cp

At further cycles The CV pattern shown in fig.4.2(A) exhibited two cathodic peaks and two anodic peaks which positions is shown in table 4.3.

Cycle	Cathodic peak	Anodic peak	Explanation
Number			
1	0.13v-0.39v(A)	0.51v-0.64v(C)	Irreversible peaks due
	0.52v-0.83v(B)		to SEI formation
2	0.24 V-0.49	0.28 V-0.47	Two step process
	V(D) & 0.62 V-	V(F) &	
	0.79 V(E)	0.62 V-0.79	
		V(G)	
3	0.33 V-0.53 V	0.16 V-0.47 V	Stable reaction
	&	&	
	0.64 V-0.79 V	0.63 V-0.79 V	
4	0.33 V-0.54 V	0.23 V-0.50 V	Stable reaction
	&	&	
	0.64 V-0.79 V	0.65 V-0.79V	

5	0.39 V-0.54 V	0.24 V-0.50 V	Stable reaction
	& 0.62 V-0.78	&	
	V	0.59 V-0.79 V	

From Table 4.3we observe that in first cycle irreversible peak indicates SEI formation. And at higher cycles two anodic and two cathodic peaks appear which indicates two step charge transfer process which are stable and reversible process. And at further cycles anodic and cathodic peaks separation decrease which corresponds to increasing reversibility. As we seen through CP and CV that charging and discharging process is highly irreversible and capacity is fading in aluminium ion battery. It indicates the less deintercalation process from SiC cathode in aluminium ion batteries.

Chronopotentiometry curve of bare SiC electrode at 13.77mA/g current density: Figure 4.3 represents the initial charge/discharge curves of the Al-ion battery using SiC as the cathode at the current density of 13.77mA/g. The cut-off voltage was set in the range of 0.02–0.8 V.

Weight of bare SiC electrode = 0.29427 g Weight of steel spacer = 0.28701 g Weight of active material = 0.00726 g Current density = 13.77mA/g (current = 100μ A) C rate = 0.45 C



Fig.4.3 Chronopotentiometry curve of bare SiC electrode at 13.77mA/g current density

Cycle	Discharge	Capacity	Charge	Capacity	Coulombic
Number	time (sec)	(mAh/g)	time	(mAh/g)	Efficiency
			(sec)		
1	8016	30.6729	247	0.9470	3.0874
2	1074	4.1106	215	0.8261	20.097
3	826	3.1635	215	0.8261	26.113
4	674	2.5792	184	0.7052	27.342
5	584	2.2367	215	0.8261	36.993

Table 4.4 Capacity of bare SiC electrode at 13.77mA/g current density

4.2 LOWER CAPACITY IN FIRST CYCLE AND CAPACITY FADING REASONS

 Formation of solid electrolyte interface on the surface of alloy: From our literature survey we found that the formation of passivating SEI films on alloy particles was confirmed by HRTEM, FTIR and XPS as a result of Lithium reaction with the electrolyte at the surface of alloy particles [69-72]. the SEI formation on alloy anodes appears to be a dynamic process of breaking off and reforming due to the constant volume changes of the alloy particles during cycling [72-74]. The thickness of SEI films and the amount of salt-degradation products have been observed to increase with the cycling number [69, 72]. Metal particles were found to catalyse SEI formation on graphite anodes [75, 76]. Therefore, the formation of SEI films on alloy anodes is expected to contribute to both the first-cycle irreversible capacity and the later cycle capacity fade [77]

- 2. Irreversible trapping of aluminium ions by host atoms [78].
- 3. Serious aggregation of alloy particles during electrochemical cycling: electrochemical aggregation has been observed in many fine-grained alloy anodes during cycling [78-81]. The reason for aggregation has been attributed to the welding effect induced by the pressure resulting from the large volume expansion. The agglomeration of active particles results in the increase of Li diffusion length and the trapping of SEI films in the particles, leading to irreversible capacity loss.
- 4. Loss of active material Because of the large volume change during cycling, cracking and pulverization of active particles and the surrounding matrix lead to the disconnection of some alloy particles from the conductive carbon or current collector [73, 82-88].
- 5. Existence of an impure phase.

4.3 COATING AS AN EFFECTIVE APPROACH TO ACHIEVE HIGHER CAPACITY (FIRST DISCHARGE) AND PREVENT CAPACITY FADING

With progress of knowledge of electrode materials, it has been found that their surface structures are of great importance to the electrochemical performance of Li-ion batteries. Carbon coating can effectively increase the electrode conductivity, improve the surface chemistry of the active material, and protect the electrode from direct contact with electrolyte, leading to enhanced cycle life of the batteries. Carbon coating together with nanotechnology provides good conductivity as well as fast Li-ion diffusion, and thus also results in good rate capabilities. The recent development of carbon coating techniques in Li-ion batteries is discussed with detailed examples of typical cathode and anode materials [89]. We are using this coating technique in our aluminium ion battery to prevent capacity fading. So we coat SiC sample and characterise it through Raman XRD and FESEM techniques.



Fig.4.4 Raman Data of as received 100 nm SiC particle and EG/SiC particle

Fig.4.4 shows the wide range $(500 - 3000 \text{ cm}^{-1})$ Raman spectra of as received and graphitized SiC (3C SiC) nano particles. SiC transverse optical (TO) phonon mode is clearly observed at ~ 787 cm⁻¹. Two specific bands namely G (~1583 cm⁻¹) and 2D (~ 2706 cm⁻¹) show the characteristic features of graphene in a typical Raman Spectra. The defect or disorder peak (D) at 1357 cm⁻¹ is coming in nano particles. The characteristics of epitaxial graphene (EG) formed on the surface of

SiC particles were analyzed ex situ with Raman system (JOBIN YVON

Ramanor HG-2S spectrometer) in backscattering configuration, under ambient conditions using an Argon laser with excitation wavelength 514.5 *nm*. The incidence laser power was 10 *mW* and the exposure time was 90 *sec*. Because the Raman signal of graphene is much smaller than that of SiC, it is necessary to use high power levels and long acquisition times. A 20X objective (NA=0.40) is used to focus the laser beam to spot size ~ 1.5 μm on the samples as well as to collect the scattered light. The spectral resolution of the Raman system is 0.5 cm^{-1} .



Fig.4.5 XRD Data of as received 100 nm SiC particle and EG/SiC particle

From fig. 4.5 XRD data(the bare SiC and EG/SiC) we can observe all the miller indices (hkl) is well matched so after coating there is no structural change. From this data we conclude that our particle structure is not damaged after graphene coating. One small A peak is present due to graphene coating. X-Ray diffraction (XRD) was performed using Rigaku smart lab ,automated multipurpose x ray diffractometer equipped with a copper target X-Ray tube with operational conditions; operational voltage of 40 kV and current of 40 mA respectively. The prepared activated carbon samples were placed inside a circular shaped sample holder. The samples were scanned between 10° to 70°.



Fig.4.6 A) FESEM Data of as received 100 nm SiC particle and EG/SiC particle

From Fig. 4.6 FESEM images of bare SiC and Graphene Coated SiC we observe that after graphene coating our surface conductivity is enhanced.

Element	Atomic%	Spec	trum 2
СК	73.79		
Si K	26.21		
		Full Scale 9974 cts Cursor: 0.000	ka\/

Fig.4.6 B) EDAX For SiC Particle



Fig. 4.6 C) EDAX For EG/SiC Particle

From the Fig 4.6 (B) & 4.6(C) EDAX data of bare SiC and graphene coated SiC we can see that the atomic percentage of carbon on surface is increased after graphene coating.

From RAMAN, XRD, FESEM, EDAX we conclude that we successfully coated graphene on bare SiC electrode.

To find the coating effect we characterise our graphene coated SiC
electrode using Chronopotentiometry and Cyclic voltammetry.

4.4 FOR GRAPHITIZED SIC CATHODE:

Chronopotentiometry of EG/SiC electrode at 5.868mA/g current

density: Figure 4.7 represents the first discharge curve of SiC in an as-

prepared cell at the current density of 5.868mA/g. The cut-off voltage was set in the range of 0.02–0.8 V.

Current density -5.868mA/g (current=25 μ A)

Weight of EG/ SiC on stainless steel spacer -0.29411 g

Open circuit potential - 0.862 V

Weight of steel spacer - 0.28701 g

Weight of active (60%) EG/SiC slurry -0.00426 g

Time for first discharge =74240 Sec



Fig.4.7(A) First Discharge cycle Chronopotentiometry curve of EG/SiC electrode at 5.868 mA/g current density

From Fig 4.7 (A) we observe that first discharge capacity of EG/SiC is 121mAh/g which is almost 25% higher than bare SiC electrode. So graphene coating is effective to enhance the first discharge capacity.



Fig.4.7 (B) Chronopotentiometry curve of EG/SiC electrode at 5.868mA/g current density

Capacity for first discharge=121.022 mAh/g

C rate=0.05 C

Cycle	Discharge	Capacity	Charge	Capacity	Coulombic
number	time (sec)	(mAh/g)	time	(mAh/g)	Efficiency
			(sec)		
1	74240	121.022	5840	9.52	7.866
2	14724	24	5226	8.56	35.667
3	11232	18.30	5616	9.154	50.021
4	8784	14.31	4860	7.922	55.395
5	7416	12.09	4572	7.453	61.646

Table 4.5capacity of EG/SiC electrode at 5.868mA/g current density

At further cycles From Fig. 4.7(B) and Table 4.5 we can see that coulombic efficiency is less so capacity fading is still remaining but first discharge capacity is enhanced due to graphene coating.

Cyclic Voltagramme and Chronopotentiometry curve of EG/SiC electrode Two cathodic and one anodic peaks were observed for the first cycle of Al-ion battery with EG/SiC cathode and AlCl₃ in the [EMIm]Cl electrolyte under the potential window of 0.8 V–0.02 V at the 0.2mV/sec scan rate. One irreversible peak observed in the first cycle due to SEI formation. Because of this irreversible charge transfer our first charging capacity is less compared to first discharging capacity causes low coulombic efficiency.



Fig. 4.8 (A) cyclic voltagramme of EG/SiC electrode at 0.2 mV/sec scan rate



Fig. 4.8 (B) First cycle Chronopotentiometry curve of EG/SiC electrode at 5.868mA/g current density

The first cycle CV peaks well fitted with CP peaks which are shown in table 4.6 which indicates a stable process in aluminium ion battery.

 Table 4.6 Comparison of CV and CP data of EG/SiC electrode at

 first cycle

	Cathodic	Cathodic	Anodic
	peak	peak	Peak
CV Peaks	.08v34v	0.56v-0.79v	0.51v75v
CP Peaks	.44v17v	0.76v-0.52v	0.58v-0.68v
	Peak match cv	Peak match cv	Peak match
	with cp	with cp	cv with cp

At further cycles two cathodic and two anodic peaks were observed for the Al-ion battery with SiC cathode and AlCl3 in the [EMIm]Cl electrolyte under the potential window of 0.8V–0.02V. The CV pattern shown in Fig. 4.8(A) exhibited two cathodic peaks and two anodic peaks at further cycles which positions is shown in table 4.7.

Table 4.7 Position of peaks for cyclic voltagramme of EG/SiC

Cycle	Cathodic peak	Anodic peak	Explanation	
Number				
1	.08v34v(A)	0.51v75v(C)	Irreversible peaks due	
	0.56v-0.79v(B)		to SEI formation	
2	0.34V-0.50V	0.05V-0.43V	Two step reaction	
	&(D)	&(F)		
	0.64V-0.78V(E)	0.63V-0.79V(G)		
3	0.39V-0.53V &	0.09V-0.42V &	Stable reaction	
	0.64V-0.79V	0.63V-0.78V		
4	0.41V-0.54V &	0.06V-0.46V &	Stable reaction	
	0.64V-0.79V	0.67V-0.79V		

5	0.44V-0.56V &	0.09V-0.46V &	
	0.67V-0.79V	0.66V-0.79V	Stable reaction

In first cycle peak is irreversible which indicates SEI formation. At higher cycles two anodic and two cathodic peaks appears which indicates reversible and stable reaction. We see this is match with CP data. At first cycle the capacity is higher rather than subsequent cycles.

Chronopotentiometry of EG/SiC electrode at 17.25mAg⁻¹ current density (current = 100 µA)

Figure 4.9 represents the initial charge/discharge curves of SiC in an as-prepared cell at the current density of 17.25mAg^{-1} . The cut-off voltage was set in the range of 0.02 V–0.8 V.

Weight of EG/SiC slurry on steel spacer=0.29667

OCP= 0.84337 V

Current density= 17.25mAg⁻1(current 100µA)

Weight of steel spacer= 0.28701 g

Weight of active (60%) EG/SiC Slurry=.005796 g

Time for first discharge=52.2390

C rate-0.33C



Fig. 4.9 Chronopotentiometry curve of EG/SiC electrode at 17.25mAg⁻¹ current density

Cycle	Discharge	Capacity	Charge	Capacity	Coulombic
number	time(sec)	(mAh/g)	time(sec)	(mAh/g)	Efficiency
1	10900	52.239	900	4.313	8.256
2	3132	15.01	936	4.486	29.887
3	2520	12.077	918	4.399	36.425
4	1998	9.575	925.2	4.434	46.308
5	1836	8.799	817	3.916	44.505

Table 4.8 capacity of EG/SiC electrode at 17.25mAg⁻¹ current density

4.5 EFFECT OF C RATE: The C rate is a measure of the rate at which a battery is charged or discharged relative to its maximum capacity. For example, a C-rate of 1 C means that the necessary current is applied or drained from the battery to completely charge or discharge it in one hour. C-rates multiples of 1 C are also exploited. In battery research, it is common to use a C-rate of 0.1 C, so to charge and discharge a battery in ten hours. Since the capacity is expressed in Ampere per hour, calculating the current necessary to charge or discharge a battery is straightforward. As it can be noticed, at slow charge/discharge rates, plateaus (red circles) along the potential plots are noticeable. These plateaus occur at potentials where two phases, i.e., a Al-rich phase and a Al-poor phase, occur in the active material at the same time. In other words, these plateaus occur at the redox potentials of the active materials, due to aluminium -ions intercalation and de-intercalation. At higher C-rates like 1 C, the time during a charge or discharge is not enough to completely intercalate and deintercalate the Al-ions, resulting in a charge and discharge states mostly due to polarization of the battery. Here, it can be noticed that at high Crates, only a small percentage of the nominal capacity is recovered.



Fig. 4.10 first discharge cycle of EG/SiC electrode at different C rate

As we can see from Fig 4.10 that at 0.05 C rate the first discharge capacity is 121mAh/g at 0.33 C rate the first discharge capacity is 52.239mAh/g. So at higher C rate the discharge capacity is lower.

4.6 EFFECT OF COATING:

We can see from fig.4.13 that the first discharge capacity of bare SiC electrode in aluminium ion battery is 97mAh/g at 25 μ Acurrent (current density=4.7mA/g) and first discharge capacity of EG/SiC electrode in aluminium ion battery is 121mAh/g at 25 μ A (current density=5.868mA/g). The capacity is increased after coating of EG because coating is helpful to prevent particle cracking and crumbling and particle aggregation and SEI formation.



Fig. 4.11 (A) Comparison of first discharge capacity of bare SiC and EG/SiC



Fig. 4.11 (B) Comparison of specific capacity of bare SiC and EG/SiC

We study from fig. 4.11(A) that at constant 25 μ A current EG/SiC discharge capacity(current density 4.7mA/g) is higher than bare SiC discharge capacity(current density 5.868mA/g) which indicates coating effect. And EG/SiC charging capacity is higher than bare SiC charging capacity. This increasing capacity after coating is constant at higher

cycles as shown in fig. 4.11(B).

4.7 FORMATION OF SOLID-ELECTROLYTE INTERFACE

(SEI) FILMS: When electrolyte contact with electrode material there is an interface formed between electrode and electrolyte called SEI formation. This SEI layer controls the reaction. In our SiC electrode in aluminium ion battery we study this SEI formation and found that after charge / discharge of battery this SEI is formed.



Fig. 4.12 A) Study morphology of EG/SiC electrode material



Fig. 4.12(B)EDAX data of EG/SiC electrode after disassembling of coin cell

From fig. 4.12(A) we can see that particle is aggregate after charging discharging. This is one of the reasons for capacity fading. And we can see SEI is formed non-uniformly on the EG/SIC electrode so active surface area is less so capacity is fading. Most of the part of SEI is formed in first cycle so a huge amount of capacity is decay in first cycle. After charging ideally there is no aluminium ion on SiC electrode but from fig. 4.12(B) EDAX we can see after charging of the cell aluminium oxygen and chlorine is deposited on the SiC electrode.

These are the components of SEI layer. Due to SEI and particle aggregation capacity of aluminium ion battery is fading.

After disassembly the coin cell in charging state EG/SiC cathode are characterized and analyzed by different characterization techniques. Morphology and particle size of as received and annealed particles which are graphitized were investigated using a Field Emission Scanning Electron Microscopy (*FESEM, Supra55, Zesiss*) with energy-dispersive X-ray analyzer. The composition of particles was analysed by energy dispersive X-ray (EDX) spectrum attached to the FESEM at a voltage of 20kV and a high probe current (up to 100nA) with high stability which corresponds to a very small beam diameter of 1nm with a short penetration depth to increase spatial resolution and minimize the background noise.

CHAPTER 5

Conclusion and Scope for future work

Currently, Li-ion batteries have been extensively investigated as the principal electrical energy storage (EES) system due to their outstanding energy and power density and it has already been commercialized for portable electronics applications. But, their main disadvantages include high cost, limited lithium resources in the earth's crust, reliability and safety. In this regard, Na⁺ ion, Mg⁺² ion and Al⁺³ ion batteries, as alternative energy storage systems have attracted significant attention among the researchers as post-lithium system. Due to the low cost, higher safety, low-flammability, lower reactivity, environmental friendliness and natural abundance of aluminium, the Al-ion battery has displayed excellent prospects. An aluminium-based redox reaction involves three electron transfers during the insertion/extraction process, provides more storage capacity relative to the single-electron transfer (Li-ion battery and Na-ion battery) and twoelectron transfer (Mg-ion battery). Additionally, the theoretical gravimetric and volumetric energy density of Al-ion battery is much higher than that of traditional Li-ion battery and other rechargeable batteries like NiCd, NiMH and lead-acid batteries. Therefore, as compared to Li-ion batteries, smaller size and lighter weight cell could be designed in case of Al-ion battery, making aluminium-ion battery a better candidate in portable electronics.

From the literature survey in Al-ion battery, it has been observed that there is an urgent need for better cathode material for the Al-ion battery system in terms of better capacity and higher safety. In my work, I take an attempt to establish SiC as a novel cathode material for Al-ion battery. SiC has higher capacity than that of graphite. Besides it is nontoxic, eco-friendly and cheap also.

It has been observed that with 4.7mA/g current density (25 μ A current), the as-prepared cell (using SiC as cathode) delivered first discharge capacity of 97 mAh/g. This is exciting result, because, the capacity is higher than that of other cathode material used for Al-ion battery, like, graphite, carbon paper, and, CuHCF. But its first columbic efficiency is

low (~ 7%). This is a challenge towards us to improve the first columbic efficiency. It has been found that, due to volume expansion, particle aggregation, less active surface area and SEI formation, its reversibility is not good. So, a thin coating on the cathode material is an effective approach to improve its reversibility and capacity also. We coated SiC with graphene layer because this graphene layer improve surface conductivity and contact of SiC cathode with steel current collector which enhance the capacity of aluminium ion battery. It has been demonstrated that epitaxial graphene on silicon carbide (EG/SiC) delivered first discharge capacity of 121 mAh/g with 5.868mA/g (25 µA current). So, with the thin coating of graphene on SiC, the first discharge capacity has been increased (almost 25%). But the cycleability problem is still there. We are further working on this problem to improve the capacity in reversible cycles. However, SiC is still promising in large-scale energy storage applications in virtue of the low cost, environmental friendliness and safety. Further we need to explore towards well suited aqueous electrolytes so that we can make more cheap, easier handling better batteries.

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