Study on new generation rechargeable thin film metal-ion battery with nano-structured electrodes: Electrical Energy Storage

M.Sc. Thesis

By

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DISCIPLINE OF PHYSICS

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Study on new generation rechargeable thin film metal-ion battery with nano-structured electrodes: Electrical Energy Storage

A THESIS

Submitted in partial fulfillment of the
requirements for the award of the degree
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AKASH DATTATRYA ATKAL

DISCIPLINE OF PHYSICS

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **Study on new generation rechargeable thin film metal-ion battery with nano-structured electrodes: Electrical Energy Storage** in the partial fulfillment 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 August 2020 to June 2022 under the supervision of Prof. Sudeshna Chattopadhyay, 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.

03/06/2022

Signature of the student with date

AKASH DATTATRYA ATKAL

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

June 3, 2022

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DEDICATED TO

MY PARENTS

Abstract

With the ever increasing global need for energy day by day, fossil-based fuels (coal, petroleum, and natural gas) as our primary energy sources are rapidly decreasing but their combustion produces more greenhouse gases and other pollutants in our environment. So as a result, there is an urgent need to seek renewable clean energy sources such as, solar energy, wind energy etc. as alternatives. Energy storage is a critical issue in enabling various renewable energy sources to be used widely. Batteries are used widely to store electrical energy in the form of chemical energy. Due to high energy and power density, Li-ion batteries have been intensively investigated as the primary electrical energy storage (EES) system. But, their main disadvantages include high cost, limited lithium resources in the earth's crust, reliability and safety. So the alternative to Li-ion battery is being explored. Due to the low cost, higher safety, low-flammability, lower reactivity, friendliness and natural abundance of aluminium, the Al-ion battery is being explored as alternative prospects. However, there is a requirement for better cathode material and separator for the Al-ion battery system in terms of better capacity, higher safety, lower cost and longer recyclability (or lifetime). Here we studied the performance of graphite as cathode against aluminium metal as anode in an ionic liquid based electrolyte using SnO_2 coated glass fiber and polypropylene separator in Al-ion and Al-air battery and comparing them with bare glass fiber and polypropylene separator respectively.

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ACRONYMS

Al	Aluminium
AIB	Aluminium ion battery
CP	Chronopotentiometry
EES	Electrochemical energy storage
Li	Lithium
LIB	Lithium ion battery
NMP	N-Methyl-2-pyrrolidone
PVDF	Polyvinylidene fluoride
OCP	Open circuit potential
XRD	X-ray diffraction
Wh	Watt hour
Emf	Electro motive force
PP	Polypropylene
SEI	Solid electrolyte interface
CV	Cyclic voltametry
GCD	Galvanostatic charge discharge

CHAPTER 1

INTRODUCTION TO BATTERY

1.1 Introduction

Energy storage plays an important role in this balancing act and helps to create a more flexible and reliable grid system. Excess electricity can be used to power storage devices when there is more supply than demand, such as during the night when low-cost power plants continue to operate.

Electrochemical energy storage-

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] The fact that both electrical and chemical energy share the same carrier, the electron, enhances this storing approach. This common point allows to limit the losses due to the conversion from one form to another.

1.2 Different components of battery:

Important components of battery-

- Anode
- Cathode
- Electrolyte
- Separator

An anode (negative electrode), a cathode (positive electrode) and an electrolyte that allows for ionic conductivity make up a battery. To prevent short circuit rigid separators (made of polymeric materials, for example PE, PP, Polyamides, Glass fibre etc.) are used which separate the anode and cathode. A battery is made of two electrochemically active couples 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 ion transport across the electrolyte ensures electro neutrality.

SEPARATOR-

Separator is one of the important component of battery and it affects its safety and performance. Understanding its properties is important for better performance. So separator analysis and characteristics must be studied.

Commercial separators are generally made up of using polyolefin polymers such as polyethylene (PE) and polypropylene (PP) have porous structures. The roles of the separator are as follows:

(1)It does not allow electrons from flowing directly through the electrolyte but provides migration path for ions.

(2) It physically prevents direct contact between a cathode and an anode, which reduces the risk of short circuits or explosions.

There are certain criteria and some properties while selecting these components.

Criteria for selection of battery electrode:

- High potential
- Limited potential variation during discharge
- Low weight, high gravimetric energy density and volumetric capacity
- Easy synthesis and processibility into practical into practical electrode
- Chemical stability towards other battery components
- Low cost
- Low toxicity

Electrolyte requisites:

- Good ionic conductivity and very low if any, electronic conductivity
- Chemical stability
- Low flammability and toxicity
- Low cost

Separator requisite:

- **Optimum Thickness**

  The separator should have of uniform thickness to have uniform ion distribution, which will result in uniform use of the active materials present in the electrode layer. Thin separators can increase energy density of batteries by giving more space for electrodes and provide short ion migration paths. Thin separators, on other hand increase the risk of punctures and short circuits. While thick separator causes high resistance and decreases the energy density. To prevent the growth of sharp dendrites, an optimal thickness should be systematically determined in the case of application.[6]

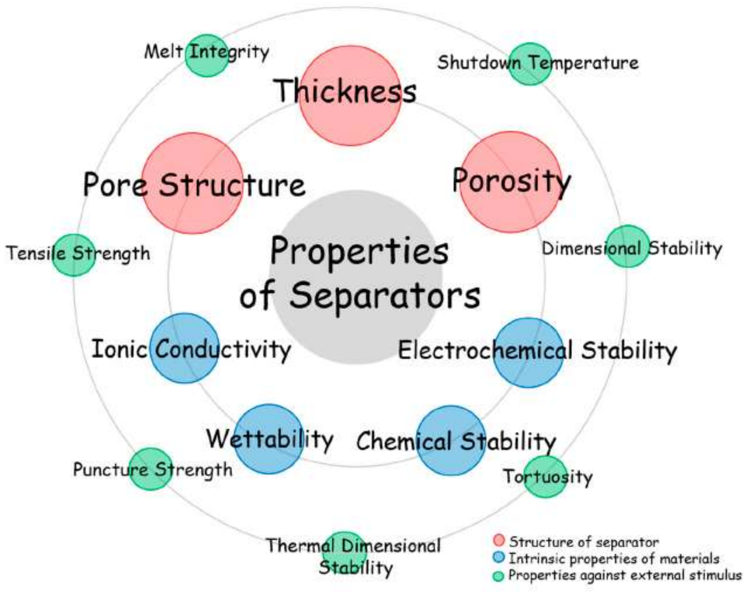

Figure 1. Illustration of the key properties of separators.

Fig. 1.1: Properties of separator

- **Optimum porosity**

  We need to consider surface properties and porous structure of separators while designing advanced separators for various battery systems as such things are important. [5]

The electrolyte can be extensively wetted into the pores with optimum porosity for facile ionic conduction. Commercial separators with pores of 1 µm or less have a porosity of ~40%.As the porosity of the separator increases mechanical strength of the separator decreases which increases the possibility of punctures. While electrolyte wettability decreases and the internal resistance increases due to low porosity. So separator should have an optimum thickness, pore size distribution and even morphology. The homogeneous pore size distribution facilitates uniform ion distribution. Pore size should be sufficient enough to absorb the electrolyte and allow ions to pass but should be less than the size of the particles of the electrode material. By comparing the weight of the liquid electrolyte before and after absorption porosity is determined. A scanning electron microscope (SEM) provide information on the surface topography and cross-section morphology of separator.[6]

- **Wettability-**

  The separator must absorb a sufficient quantity of electrolyte, and pores must hold the absorbed electrolyte during cell operation. When the wettability of the separator is high cell performance is improved along with reduction in ionic resistance of the cell. high which improves the cell performance. Low wettability, On the other hand, causes dendritic growth due to non-uniform ion distribution, preventing electrode materials from being completely used. So, wettability is essential for both cell capacity and life cycle. Degree of the wettability is indicated by the contact angle measurement between electrode and electrolyte. By observing shape of electrolyte droplet with time placed on a dry separator contact angle is measured. A contact angle of more than 90° is implication of poor wettability, while contact angle lower than 90° implies greater affinity between separator and electrolyte.[7]

For facile ion conduction which result in lower internal resistance, high wettability between separator and electrolyte is necessary.

- **Ionic conductivity**

  The ionic conductivity of an electrolyte separator should preferably be in the range of 10^{-3} to 10^{-1} S cm^{-1}. Commonly we use MacMullin number to predict ionic conductivity of the cells. The MacMullin number is the ratio of the separator resistance to the electrolyte resistance when wetted with electrolyte. The lower the MacMullin number, the more efficient and safe the cell.[7]

- **Chemical and Electrochemical Stability-**

  The separator must be an electronic insulator.[5] It should also be electrochemically stable when exposed to redox reaction potentials. We can obtain electrochemical redox processes by using cyclic voltammetry or linear sweep voltammetry to predict the separator's stability. [7]

- **Thermal Stability**

  The separator's thermal stability should be maintained throughout a wide temperature range. [6] The melt integrity and "shutdown function" are used to determine the separator's thermal stability. the temperature at which the separator's mechanical properties are no longer maintained called as the melt integrity temperature, and the ideal melt integrity temperature is 200°C or greater.[6] Under unusually high temperatures, the separator begins to melt. As a result, ion conduction is prevented by blocking pores. This process is called the shutdown function. When the polymeric separator reaches the shutdown temperature, it begins melting the pores and preventing ionic flow. To prevent contact between electrodes after shutdown, mechanical integrity must be maintained.[8]

- **Dimensional Stability**

  In commercial-grade separators, shrinkage in all directions should be less than 5%. The shrinkage is calculated by comparing the areas of the original separator with the areas of the separator after it has been impregnated with liquid electrolyte for a few hours. Thermal shrinkage should also be less than 5% after 60 minutes at 90°C.

- **Mechanical Properties**

  The separator's mechanical properties must be sufficient to sustain physical stress induced by external compression and electrode expansion. When a typical separator is immersed in an electrolyte, its mechanical properties change. As a result, mechanical stability must be taken into account while designing a high-stability separator.[8]

- **Limitations of separator**

  In batteries, polyolefins, particularly PE and PP, are commonly employed as separators. Polyolefin is a mechanically strong, chemically stable, and cost-effective material. Because of its large pore volume and size, its conductivity rises after being soaked in an electrolyte. However, polyolefin has some intrinsic features, such as low wettability and poor thermal stability. Thermal shrinkage can occur at high temperatures because to low thermal stability, resulting in a short circuit. At high charge/discharge rates, the low wettability might result in over potential and capacity deterioration. [8]

Li-ion batteries have been a cornerstone for EES due to their remarkable energy and power density [9-11]. However, concerns about the expensive cost and limited Li supplies in the earth's crust have prompted researchers to look for more environmentally friendly alternative energy storage methods [12-14].

The use of sodium-ion and magnesium-ion batteries as innovative energy storage methods in portable gadgets has piqued the interest of researchers. Recently, the feasibility of an Al-ion battery (AIB) with multivalent metal ions transmitting internally has been investigated. The Al-ion battery has a bright future because of its low cost, ease of use, and high security. However, the capacity and the cycle life are not satisfying at present.

When compared to LIBs, AIB is more advantageous in terms of cost, environment, and safety in terms of practical use. To begin with, Al is substantially less expensive than Li and can be recycled.

Given the billions of little LIBs consumed each year in phones and computers, AIB technology could be revolutionary if performance can be improved any more. Second, Li is toxic and flammable in air, but Al is neither toxic nor flammable. As a result, the usage of AIBs would aid in the elimination of environmental issues generated by the disposal of LIBs.

Furthermore, unlike traditional LIBs that use a highly flammable organic electrolyte, this new AIB system will not catch fire because the electrolyte is essentially a liquid salt at room temperature. Another notable benefit of the new AIBs is their adaptability. This AIB system can be sculpted or moulded with varied sizes to fulfil different applications such as wearable electronics, as illustrated in a polymer-coated pouch cell.

As a result of its great energy and power density, Li-ion batteries are being extensively explored and used. Their shortcomings, such as cost, lithium resource, reliability, and safety, are clear. Al-based batteries is becoming one of the alternatives for energy storage devices due to its natural abundance and affordable cost.

The Al–ion battery system is being studied for many years; however, due to the rapid corrosion and hydrogen evolution reaction between Al and the electrolyte, the electrode's use is lowered, and the battery is eventually scrapped. An Al-ion battery containing multivalent metal ions transmitted internally, such as VO_2, V_2O_5, anatase TiO_2 in aqueous solution, polymers, copper hexacyanoferrate, and prussian blue analogues, has recently gained a lot of attention.

However, most of them doesn’t show satisfactory performance including their low capacity, short cycle life or low voltage plateau. We established a new kind of Al-ion battery with graphite as a cathode material and separator modified Al-graphite battery, Al-air battery. In this study, briefly the goal is to learn about the rechargeable metal-ion battery (beyond lithium-ion battery), thin-film-battery and physics behind their applications.

CHAPTER 2

2.1 Working principle of battery:

The basic concept of electrolytes and electron affinity should be thoroughly understood before comprehending the basic principle of a battery. There will be a potential difference between two dissimilar metals or metallic compounds when they are submerged in an electrolyte. Certain substances produce negative and positive ions, when dissolved in water, according to research. An electrolyte is a sort of chemical like this. Electrolytes include all types of salts, acids, and bases, among other things.

The amount of energy liberated when electron is added to a neutral atom to form negatively charged ion is called as electron affinity. Electron affinities for different material are different which depend on structure of material. When two different kinds of metals or metallic substances, called electrodes, are immersed in the same electrolyte solution, one of them will release electrons gain and the other will electrons. Depending upon the electron affinities of these metals or metallic compounds one metal (or metallic compound) will lose electrons and other one will gain them. The metal having low electron affinity will gain electrons from the negative ions of the electrolyte in the 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. As a result, there will be a difference in electron concentration between these two electrodes. 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. The cathode form negative terminal whereas anode form positive terminal and the difference between the potential of these two electrode gives rise to open circuit voltage.

In a battery system, oxidation reaction takes place at anode whereas reduction reaction takes place 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.

$E_{cell}= E_{pos} - E_{neg}(V)$

However real voltage varies with factors as temperature and concentration of active materials.

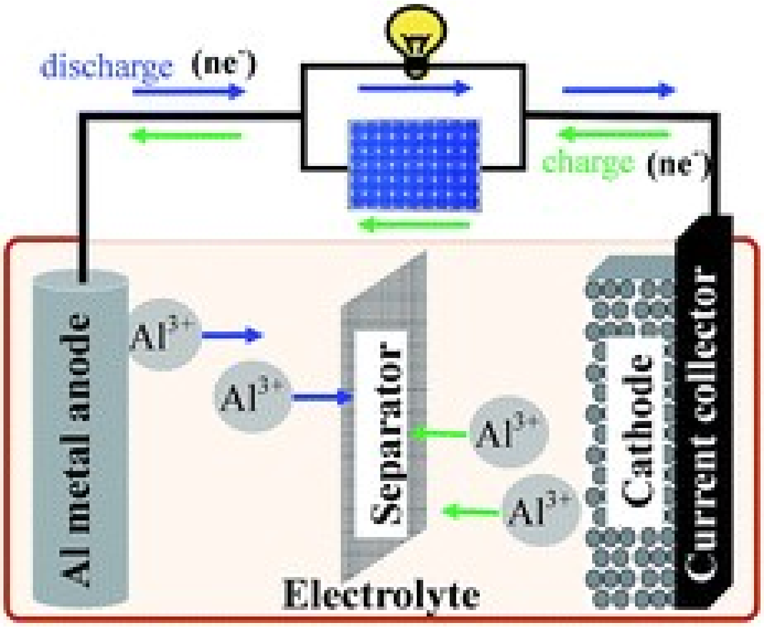

Fig. 2.1: Schematic of Al-ion battery

2.2 Parameters used to measure battery performance:

Battery Capacity: Battery capacity is a measure of charge stored by electrode and Determined by active material present in electrode. It represent maximum amount of energy that can be extracted from the battery.[15]

Coulombic efficiency: Coulombic efficiency is ratio of total charge extracted from battery to total charge put into the battery over full cycle. CE= Charge delivered during discharge/charge stored during charge& is indication of reversibility of electrode reaction.

Energy density (by weight and by volume): The gravimetric energy density or the specific energy of a battery is amount of energy battery can store in comparison to its weight and its unit is Watt-hours/kilogram (Wh/kg)**.** The volumetric energy density or energy density of battery is amount of energy battery can store in comparison to its volume and its unit is watt-hours/litre (Wh/l). [16]

Battery Voltage: The voltage of a battery originates from the difference in the electrochemical potentials of the cathode and anode.

Cycle Life: The cycle life of batteries is the number of charge and discharge cycles that a battery can complete before losing performance.

C-rate is the speed at which battery is charged relative to its battery capacity.

Power density: The power density is the power that can be derived per unit weight of the cell (W/Kg).

2.3 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 used hot air over for drying our samples at 50˚C to 70˚C.

Fig. 2.2: Hot air oven

2. Argon filled glove box:

A glove box is a completely airtight sealed container. It has an enclosed working area on the inside which is completely isolated from the outside. It's designed as an inert gas glove box to keep an artificial atmosphere inside it, usually consisting of pure argon or pure nitrogen with a low pressure.

Oxygen and water vapour concentrations are normally below 1 ppm.

It is used to protect the sample, which is being handled inside the box from the outside, in particular from unwanted reaction with oxygen and/or water vapour.

The box is mostly made of stainless steel, with a polycarbonate window and gloves from butyl. The glove box system is based on the principle of gas circulation, which means that the working gas is constantly circulated between the glove box and the gas purifier. Moisture and oxygen are removed from the inert gas glove box atmosphere by the gas purification system. It draws oxygen from the inert gas using an unique reactive agent. Water is removed using a patented adsorbent. The gas purification system can be regenerated in a PLC-controlled process by passing a regeneration gas through it when it becomes exhausted.

Table 2.1: Function of glove box and its parts

Sr.No.	Part	Function
1	Glove box	airtight sealed working space
2	Window with Glove Ports and Gloves	Used to work with samples inside box
3	Control	Central controlling and monitoring the system.

	Panel	Accessing system functions and system parameters
4	Antechamber	Used to transfer material in and out of the box
5	Main switch	Used to turn on and off to the box
6	Gas Purification System	By continuous circulation over the reactor it removes water, oxygen from the inert gas. By continuous circulation over solvent removal filter it removes solvent vapors from the inert gas.
7	Vacuum Pump	• to evacuate the antechamber • to reduce the box pressure • during the regeneration cycle
8	Flow Meter	Indicates the flow of the regeneration gas during a regeneration cycle.
9	Electrical Cabinet	Contains electrical and electronic components. Should not be opened(opened by maintenance person only)
10	Footswitch	Used to increase and decrease the box pressure

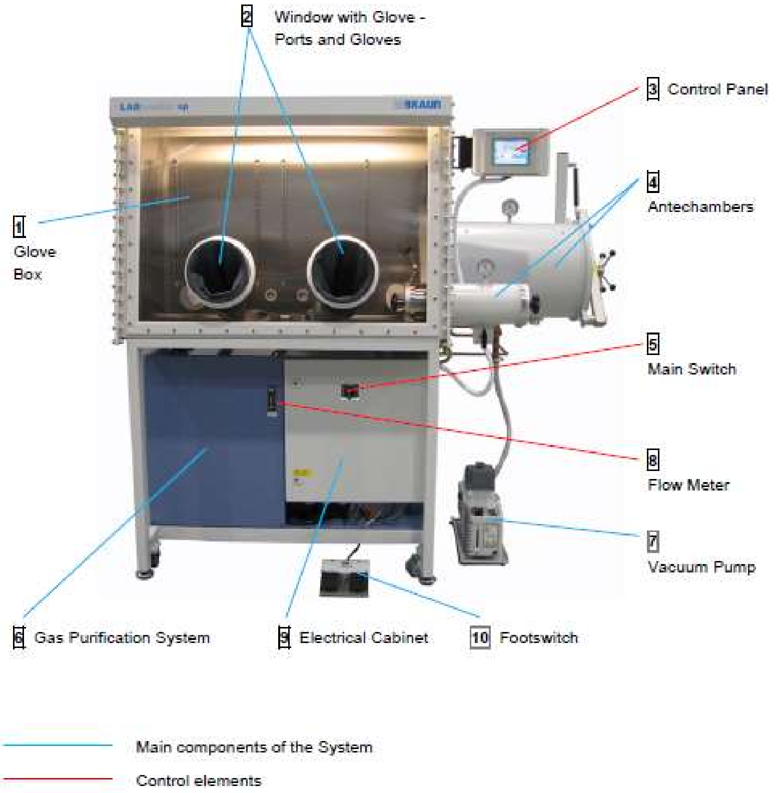

Fig. 2.3: Argon filled glove box

3. Magnetic stirrer:

A magnetic stirrer is a laboratory instrument that creates a spinning magnetic field using either a revolving magnet or stationary electromagnets. 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 is frequently equipped with a heating element. In the laboratory, stirrers are frequently utilised. We may change the speed of our stirrer from 50 to 1500 revolutions per minute. Because just an inert magnet bar, which is readily cleaned, is placed into the sample/fluid, magnetic stirrers reduce the danger of contamination. Furthermore, for constant, repeatable mixing or combining over long time scales, using a magnetic stirrer rather than human stirring is crucial.

Fig. 2.4: Magnetic stirrer

4. 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

4.1 Cyclic voltammetry:

Among electrochemical methods, cyclic voltammetry has long been a fundamental analytical tool. CV has the following advantages over other measurements:

1) It is feasible to determine whether the reactants' chemical reaction is reversible or irreversible. Due to the over potential, the cyclic voltammogram of a quasi reversible process shows incremental peak changes to higher potential values when the scan rate is increased.

2) It is possible to identify the voltage at which an oxidation or reduction reaction happens.

3) For the substances of unknown concentration quantitative analysis can also be done.

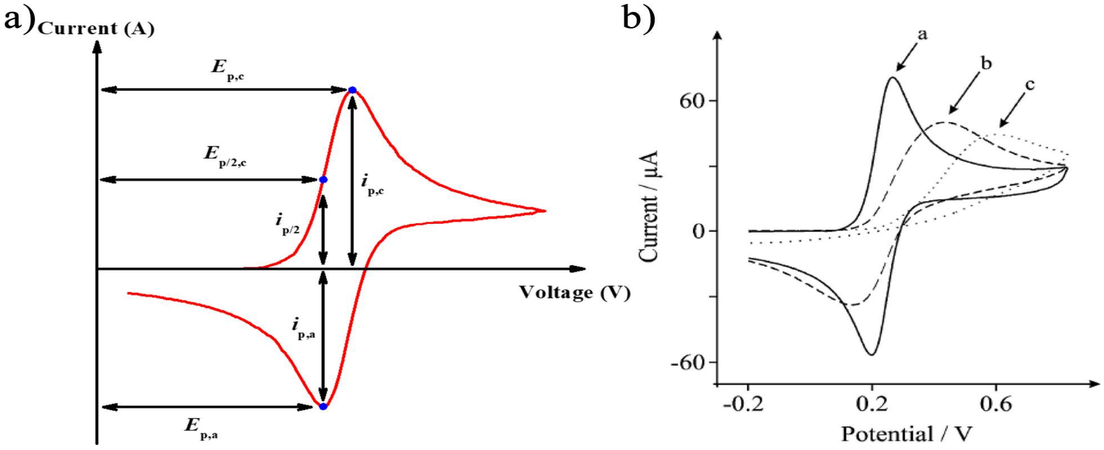

Figure2.5: a) An example of cyclic voltammogram and b) cyclic voltammogram in case of reversible, quasi-reversible and irreversible electron transfer.

Using CV we can calculate,

1) Electrochemical reactivity of material can be obtained.

2) Scan rate can be measured (rate of voltage change over time).

3) Diffusion coefficient can be measured.

4) Specific capacity can be estimated using the formula,

$Q(\text{mAh/g})=\int_{E1}^{E2} \mathrm{i(E)dE} \;/\; (2 \times 3.6)\mathrm{mv} \int_{E1}^{E2} \mathrm{i(E)dE}$

is the total charge storage obtained by integration of cathodic and anodic regions in the cyclic voltammograms i.e. area under CV curve, m is the mass of active material in grams, and v is the scan rate.

Depending on the scan rate employed in CV, the redox system can display a reversible, quasi-reversible or totally irreversible behavior. since v brings about the time available for the electrode-solution interphase to attain the equilibrium condition dictated by the Nernst equation. It is convenient to rationalize such a dependence by the dimensionless parameterΨ in Eq. below which compares the standard heterogeneous rate constant k_{sh} of the specific electron transfer with the scan rate$v$:

$$\Psi = \frac{\gamma^{\alpha} k_{sh}}{(\pi a D_o)^{1/2}}$$

Where,

$\gamma = (\frac{D_O}{D_R})^{1/2}$-square root of the ratio between diffusion coefficients of oxidized (D_O) and reduced (D_R) partners

α - charge transfer coefficient

a= nFv/RT - normalized scan rate

This definition of Ψ applies to only for reduction processes in case of oxidation reactions D_O is replaced by D_R. A charge transfer is thus defined totally irreversible for $\Psi < 10^{-3}$, quasireversible for$7 > \Psi > 10^{-3}$, and reversible for Ψ>7.[17-18]

Two peaks in the voltammogram means our redox couple undergoes two sequential electron transfer reaction.

4.2 Galvanostatic charge and discharge:

This test involves applying a constant current through the cell and watching the voltage change over time. The step is called a "charging" phase if a positive current is delivered, and the voltage is intended to progressively increase. A negative (or "discharging") current, on the other hand, is intended to lower the voltage. The current is reversed as soon as a predetermined voltage is attained, and the next stage begins. A full cycle consists of a charging and discharging operation; typically, a series of cycles is undertaken to measure performance variance over consecutive cycles. A newly built device may be discharged or charged, depending on the presumed electrochemical reactions taking place in the device. Therefore, depending on the initial state of the cell, the cycling should be started with either a charging or a discharging step accordingly and calculated using formula.

$C_{step} = t_{step} * i_{step} / m_{electrode}$

Where,

$C_{step}$is the specific capacity of a given step,

t_{step} is the charging or discharging time of that step,

i_{step} is the applied current in that step, and

$m_{electrode}$is the mass of active material in the electrode

Coulombic efficiency, specific capacity can be measured using .
galvanostatic charge discharge.[18]

2.4 Why Aluminium?

Lithium is present in the earth's crust at 0.002–0.006 wt%. It is the 33rd most abundant element in nature and is distributed widely in trace amounts in rocks, soils, and surface, ground, and sea waters.

The abundance of aluminum is around 8 wt.-%, which is most abundant metal in the earth's crust and the third most abundant element after oxygen and silicon. Also the cost per kg of Li is very high than that of Al. The specific volumetric capacity of an Al is about 8046mAh/ cm^3 almost four times higher than that of Li which is about 2062mAh/cm^3, while gravimetric capacity (2980mAh/g) is comparable to that of Li metal (3860mAh/g).[19]

2.5 Review of Past Work and Problem Formulation:

The researchers are working on AIB since 1990, but they came up with the problem of electrolyte and suitable cathode material. With the advent of suitable electrolyte in 2011 various research group shown interest in AIB.

In 2011, N. Jayaprakash et al., introduced a rechargeable Al-ion battery using V_2O_5 as a cathode, Al as an anode and $AlCl_3$ in [EMIm]Cl as the electrolyte. For the first time, they had reported the discharge capacity of approximately 305mAh/g which remains 273mAh/g after 20 cycles.[20]

Further, in 2012, S. Liu et al., used TiO_2 nanotubes as a potential cathode material or Al-ion battery. The electrochemical Al storage of anatase TiO_2 nanotube arrays in $AlCl_3$ aqueous solution was investigated. It is firstly demonstrated that Al-ions can be reversibly inserted/extracted into/from anatase TiO_2 nanotube arrays in $AlCl_3$ aqueous solution due to the small radius steric effect of Al-ions. The maximum discharge capacity of 75mAh/g is obtained. [21] In 2013, another research group used fluorinated natural graphite as cathode and Al as anode in an ionic liquid (1,3-di-n-butylimidazolium Bromide [bim][Br]) based electrolyte and this battery showed stable electrochemical behaviour with a discharge capacity of 225mAh/g [22]. In the same year, W. Wang et al., developed Al-ion battery using VO_2 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 165mAh/g in the initial cycle and 116mAh/g after 100 cycles [23]. 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-3-methyl imidazolium chloride as a solvent with a molar ratio of 1.3:1. At the current density of 50mA/g, the discharge capacity is 84.55mAh/g over 50 cycles. Even at a high current density of 150mA/g , the discharge capacity still remains 62.71mAh/g over 50 cycles [24]. S. Liu.et al., in 2015, developed an Al-ion battery with copper hexacyanoferrate in acidic aqueous $Al_2(SO_4)_3$ solution. A specific capacity of 62.9mAh/g obtained at the current density of 50mA/g [25]. 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 well defined discharge voltage plateaus near 2 volts, a specific capacity of about 70mAh/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 4,000mA/g (equivalent to 3,000 W/kg), and to withstand more than 7,500 cycles without capacity decay. [26]

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, 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. Also, looking into various alternative of separator and modified separator.

CHAPTER 3

Experimental Details

3.1 Sample preparation

Binder preparation: PVDF is most commonly used binder as 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. We took PVDF 6 wt% of NMP. Ultra-sonication was done for mixing of PVDF in NMP till uniformity is obtained. 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.

Cathode material preparation: For our cathode electrode we use graphite as the active material. We prepared slurry using active material and binder (PVDF+ NMP) in a weight ratio of 80:20. As we are using graphite a allotrope of carbon as cathode so no need of using conductive carbon. For uniform mixing of this slurry, we mix it using magnetic 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 copper foil (used as current collector).

We dry this slurry using hot air oven for three hours at a temperature of 50-60ºC. And then cut into 15mm diameter using disc cutter.

SnO_2 coated PP and glass fibre separator:

SnO_2 coating increases mobility of ion by increasing wettability. The SnO_2-modified PP and glass fibre Separator was synthesized by a blade coating procedure(coated on one side). Binder (PVDF+NMP) already prepared used for preparation of SnO_2slurry. The commercial polypropylene separator was modified by coating of a slurry (90 wt% SnO_2 and 10 wt% PVDF in NMP) on one side of the PP separator, then dried at room temp for 24hrs.

Size of SnO_2 nanoparticles should be larger than the pore size of the separator otherwise the nanoparticles would penetrate into the pores of the separator and will create hindrance in the diffusion of Li^+.[27]

Electrolyte preparation:

Due to the hygroscopic nature of the$AlCl_3$, electrolyte has been prepared inside the glove box where the oxygen and water vapour level is less than 0.5 ppm is maintained. The ratio of salt$AlCl_3$ to 1-ethyl-3-methyl-imidazolium chloride ([EmIm]Cl) solvent was taken in molar ratio 1.3:1. [EmIm]Cl is used as solvent. We mix slowly$AlCl_3$ into [EmIm]Cl because this process is exothermic. Initially both salt and solvent are in solid form but after mixing due to exothermic process and low melting points they show a phase change and convert into liquid phase. After that we did magnetic stirring for 30 minutes for proper mixing.

The as-prepared electrolyte is kept inside the glove box. [28,29]

3.2 Coin cell assembly:

We assembled our 2032 type coin cells inside the glove box. First we inserted all the components-

Separator(glass fibre), cathode (graphite slurry on copper foil of 15mm diameter), stainless steel spacer, spring(to make coin cell compact) and tweezers inside the glove box. We used electrolyte between the anode and cathode. Spacer and spring for tight binding of coin cell. Spacer also act as current collector. 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 of the glove box.

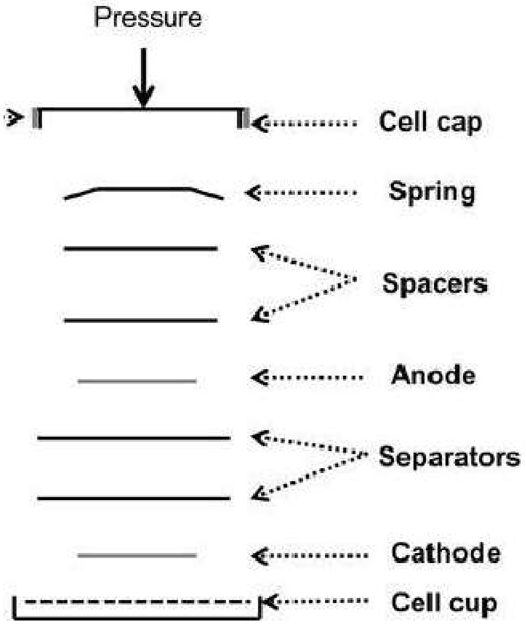

Fig.3.1: Coin cell assembly steps

Coin cell testing: We used electrochemical analyzer 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 while black wire is used for grounding. The results have been discussed in next chapters.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Aluminum ion battery: Working Mechanism

To date ionic liquids have been used as an electrolyte to realize an Al metal-based battery. Two different mechanisms are explained for an ionic liquid electrolyte according to the cathode material used. The working principle for an aluminium ion battery in an ionic liquid is that aluminium ions (Al) are formed after getting oxidized at the anode where these ions form a complex ion$Al_2Cl_7^-$ with$AlCl_4^-$ in the electrolyte. These$Al_2Cl_7^-$ anions will dissociate at the cathode electrolyte interface and help in the intercalation of Al^{3+} ions into the cathode during charging. During discharging this Al^{3+}ions will be de-intercalated from the cathode interstitial space and will be carried to the negative electrode by the $AlCl_4^-$ anions. [30]

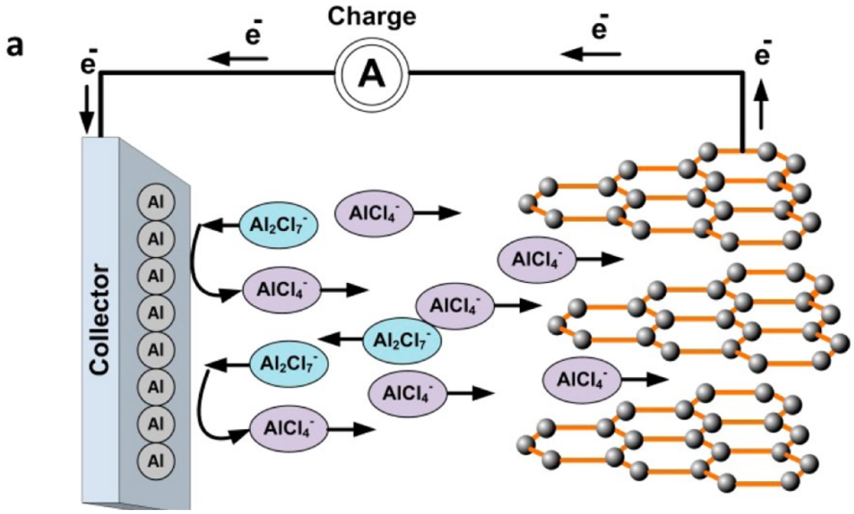

Fig.4.1: Al-graphite battery Schematics of the charging process.[30]

Electrode reactions for Al-ion battery-

During Charging Process:
Positive Electrode: $nC + AlCl_4^- \longrightarrow C_n[AlCl_4] + e^-$
Negative Electrode: $4Al_2Cl_7^- + 3e^- \longrightarrow Al + 7AlCl_4^-$

During discharging process:
Positive Electrode: $C_n[AlCl_4] + e^- \longrightarrow nC + AlCl_4^-$
Negative Electrode: $Al + 7AlCl_4^- \longrightarrow 4Al_2Cl_7^- + 3e-$

The reactivity of chloroaluminate with the polymers used as separators and polymeric binders in batteries is another important aspect of chloroaluminate-based systems. Elia et. al tested the chemical stability of a number of separators used in Li-ion battery applications against chloroaluminate melts. Their research revealed that traditional polymers such as polypropylene, polyethylene, polyvinyl alcohol, and polyimide are unstable, reducing the number of potential choices for Al-ion cell construction. [31]

4.2 Electrolyte uptake comparison:

For Electrolyte uptake

$Electrolyteuptake = \frac{W_t - W_o}{W_o} * 100\%$ ……………………[32]

Where,
W_o- the mass of the original separator
W_t- the mass of the separator after the liquid electrolyte is completely absorbed.

For bare PP	for SnO_2 coated PP
W_0- 24.3 mg	26.9mg
W_{50} – 37.4 mg	55.1mg
W_{100}- 42.0 mg	76.1 mg
W_{150}- 49.1mg	89.7mg
W_{200}- 51.6mg	92.5mg

Table 4.1: Comparison of electrolyte uptake

Time(sec)	**Electrolyte Uptake(%)**	
	Bare PP	**SnO_2 coated PP**
0	**0**	**0**
50	**53.90**	**104.83**
100	**74.49**	**182.89**
150	**102.05**	**233.15**
200	**112.34**	**243.86**

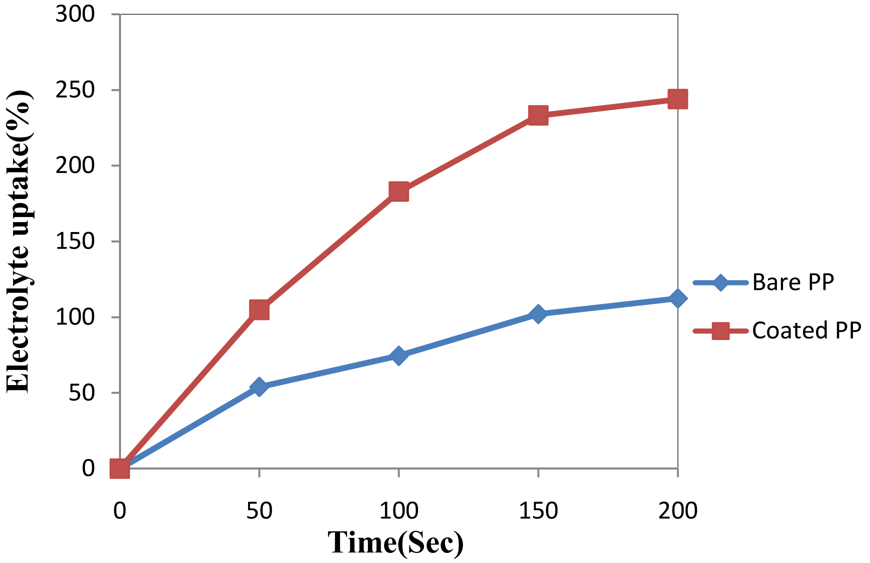

Fig.4.2: Effect of wetting time on electrolyte absorption by membrane

4.3Chronopotentiometry curve

4.3.1 Chronopotentiometry of Al-graphite battery-

Weight bare Cu foil(15mm dia.)- 15.38 mg

Weight of graphite(with PVDF and NMP as binder) loaded Cu foil- 24.83 mg

Weight of electrode material- 9.45 mg

Weight of active material – 9.45*0.8=7.56 mg

The OCP was found to be 0.802V.OCP contains information using which battery state of health and state of charge can be estimated. OCP vs Time plot shows that the OCP is constant over long period of time which means battery is stable over the period.

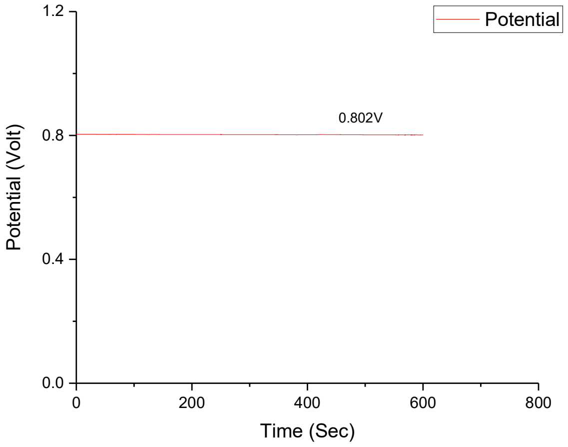

Fig. 4.3: OCP Vs Time for Al-graphite battery

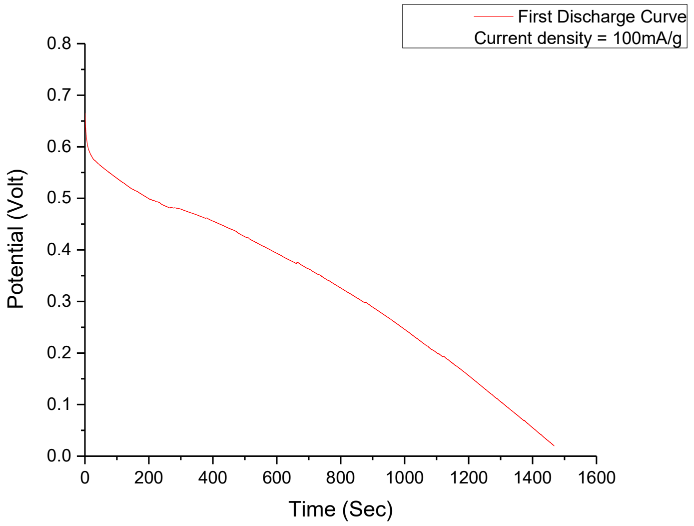

Fig.4.4: Chronopotentiometry curve for first discharge of Al-Graphite battery at 100mA/g current density

From Fig.4.4 we calculated the first cycle discharge capacity and found to be 51.38mAh/g at current density of 100mA/g.

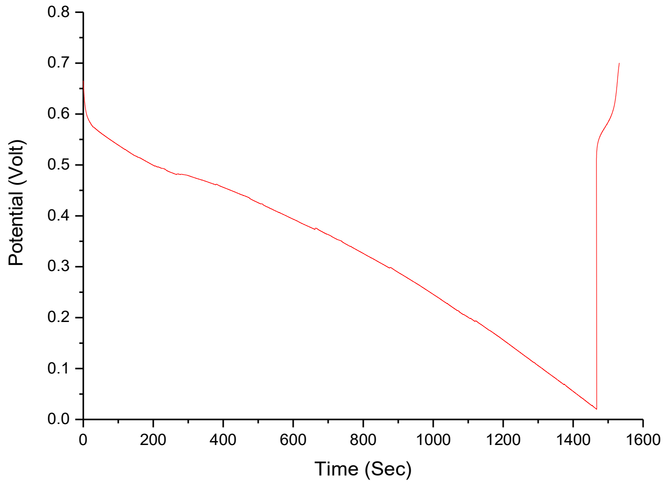

Fig.4.5: Chronopotentiometry curve for first cycle of Al-Graphite battery at 100mA/g current density

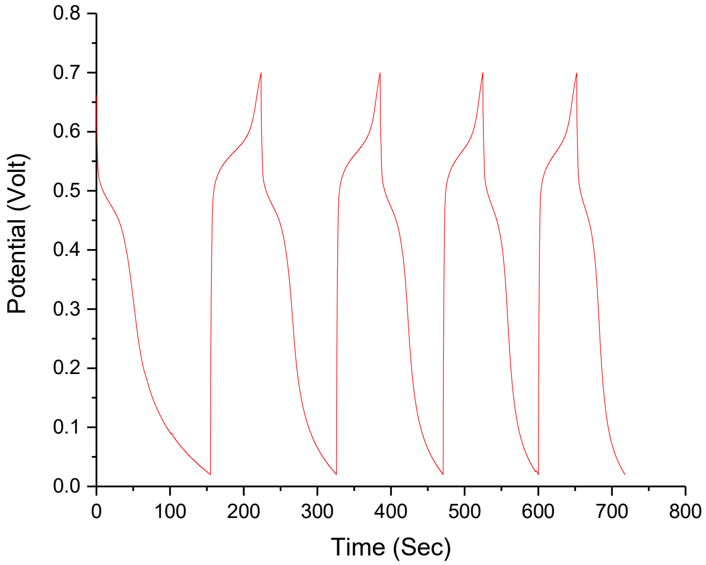

Fig. 4.6: Chronopotentiometry curve of Al-Graphite battery from second cycle onwards at 100mA/g current density

Table 4.2: capacity of Al-Graphite battery at 100 mAh/g current density

Cycle number	**Discharge time(sec)**	**Discharge Capacity (mAh/g)**	**Charge time(sec)**	**Charge Capacity (mAh/g)**	**Coulombic Efficiency**
1	1467	51.38	65	2.28	4.41
2	220	5.38	289	2.398	44.57
3	391	3.56	450	2.07	58.15
4	536	2.96	590	1.88	63.51
5	665	2.62	717	1.81	69.08

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

And from table we see that the first columbic efficiency is 4.41% which indicates highly irreversible process and less deintercalation process result capacity fading in subsequent cycles columbic efficiency increased to 69.08% 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.

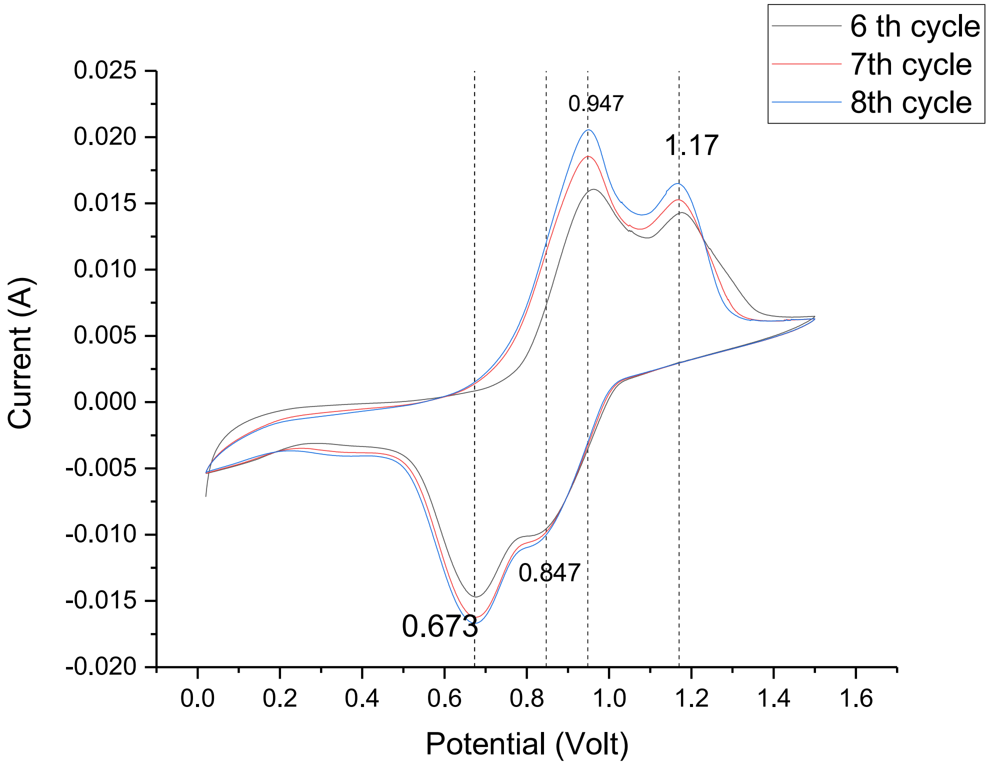

Fig. 4.7: Cyclic voltammogram of Al-graphite battery at scan rate 5mV/s

CV curve shows that as there are two peaks which means in our system Al undergoes two sequential electron transfer reactions. Also even after cycles the oxidation and reduction peaks occurs at same place indicates the reversibility and stability of system.

Area under CV curve 0.013394, so using formula

$Q(mAh/g) = \int_{E1}^{E2} i(E)dE \; / \; (2 \times 3.6)m\nu$

Q= 0.013394/(2*3.6*0.00756*0.005)Q= 49.21mAh/g

Specific capacity of the battery found to be 49.21mAh/g at current density of 100mA/g which is almost equal to that of calculated from gcd curve. (Compared with Al-Natural graphite battery at 99mA/g is 110mAh/g).[30] One of the reason for less capacity when compared to literature is active material(graphite) loaded on cathode so by using various thin film deposition techniques further we will try to improve capacity of battery.

4.3.2 Chronopotentiometry of Al-Graphite battery (with SnO_2 coated separator)

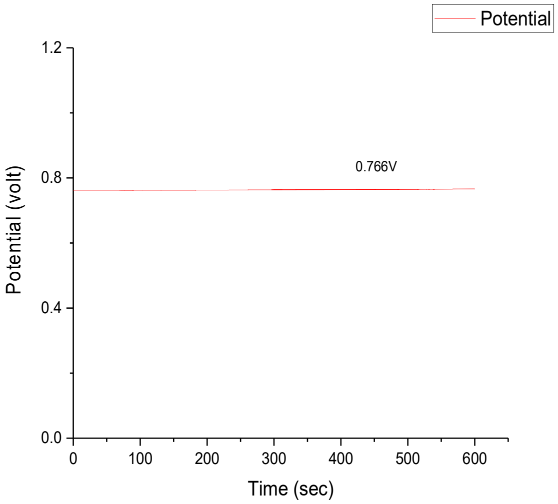

Fig. 4.8: OCP Vs Time for Al-graphite battery (with SnO_2 coated separator

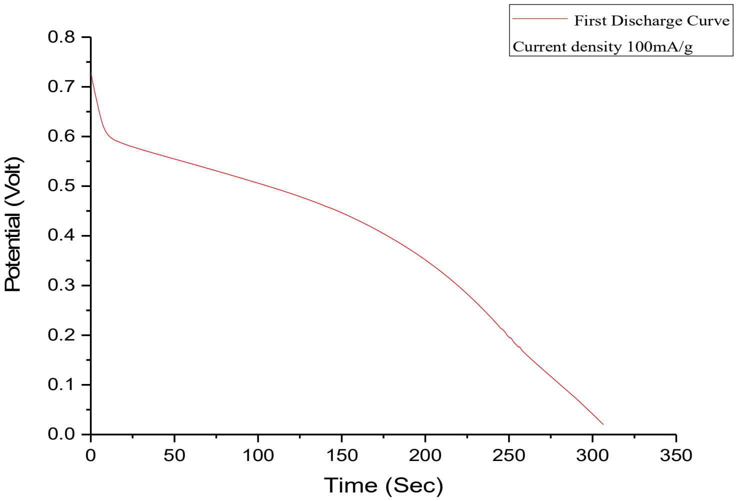

Fig. 4.9: Chronopotentiometry curve for first discharge of Al-Graphite battery (with SnO_2 coated separator) at 100mA/g current density.

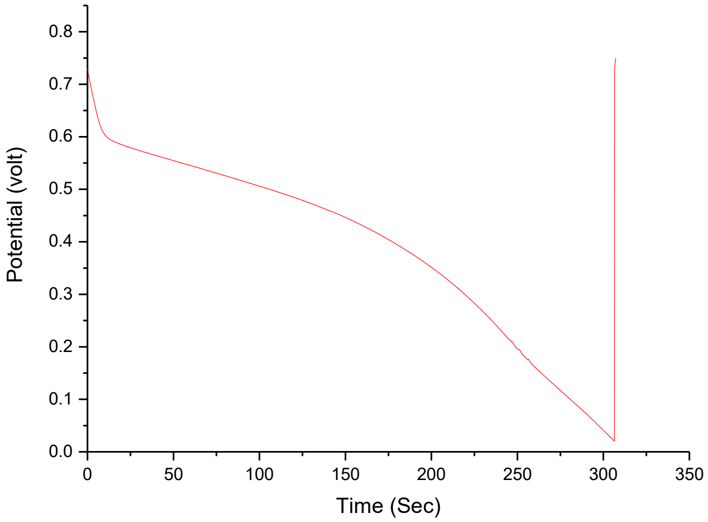

Fig. 4.10: Chronopotentiometry curve of first cycle of Al-Graphite battery (with SnO_2 coated separator) at 100mA/g current density

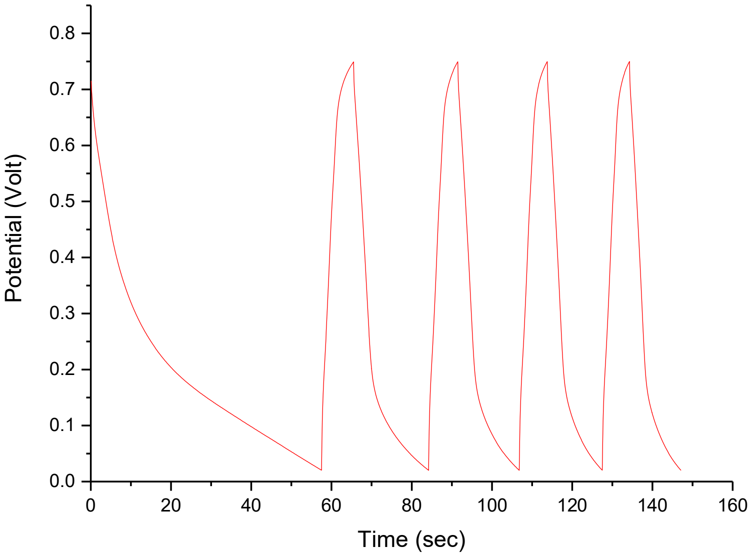

Fig. 4.11: Chronopotentiometry curve of Al-Graphite battery second cycle onwards (with SnO_2 coated separator) at 100mA/g current density

Table 4.3 Capacity of Al-Graphite battery (with SnO_2coated separator) at 100mAh/g current density

Cycle number	Discharge time(sec)	Discharge Capacity (mAh/g)	Charge time(sec)	Charge Capacity (mAh/g)	Coulombic Efficiency
1	306	10.66	0.8	0.278	2.608
2	58	1.997	66	0.282	14.26
3	84	0.64	92	0.258	40.31
4	107	0.529	114	0.247	46.69
5	128	0.473	135	0.240	50.73

We found that Al-ion battery made using SnO_2 coated glass fibre has less capacity when compared with battery made using bare glass fibre. As the size of SnO_2 particle was less (100nm) compared to pores of glass fibre it might be possible that it may penetrate into the pores of glass fibre which created the hindrance to the diffusion of ions.[29]

4.3.3 LOWER CAPACITY IN FIRST CYCLE AND CAPACITY FADING REASONS

1. According to literature review, The formation of passivating SEI films on electrodes was confirmed by HRTEM, FTIR, and XPS as a result of lithium reaction with the electrolyte at the surface of alloy particles,. The cycling number has been found to increase the thickness of SEI films and the amount of salt-degradation products. 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.[33]
2. Irreversible trapping of aluminium ions by host atoms.[34]
3. 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.[34]

4.3.4 PLETEAU FORMATION: Further during discharge cycle the slopes were not linear and different plateaus were seen in Voltage (V) vs time(t) graph, this non linear slopes showed that the movement of ions have different coexisting phases. These plateaus occurred at potential where two phases i.e. ion rich phase and poor ion phase, occurs in the active material at the same time, in other words these plateau occur at the redox potential of active material due to intercalation and de-intercalation. Plateaus can be seen in both charge and discharge cycle of both separator coated Al-graphite battery and bare separator Al-graphite battery but the slope of discharge plateau was much steeper in both separator coated Al-graphite battery as seen in compared to bare separator Al-graphite battery.

4.4 Al-air batteries-

By the reaction of Al and oxygen Al-air battery produces electricity. They have highest energy densities amongst all batteries but are not widely used because of high anode cost.

Aluminium-air batteries are primary cells i.e. they are non rechargeable. As the aluminium anode is consumed by its reaction with atmospheric oxygen at cathode immersed in water based electrolyte to form hydrated aluminium oxide, so battery will no longer produce electricity. So need to replace anode every time after discharge.

A polypropylene based Al-air battery is constructed using aluminium foil as anode, graphite as cathode and PP as separator. [35]

We demonstrate an improved and inexpensive paper-based aluminum-air battery employing KOH/NaOH as the electrolyte with sufficient energy to power small devices.[36]

Cathode reaction-

$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

Anode reaction-

$Al \longrightarrow Al^{3+} + 3e^-$

$Al^{3+} + 4OH^- \longrightarrow Al(OH)_4^-$

Overall reaction

$4Al + 3O_2 + 6H_2O \longrightarrow 4Al(OH)_3$

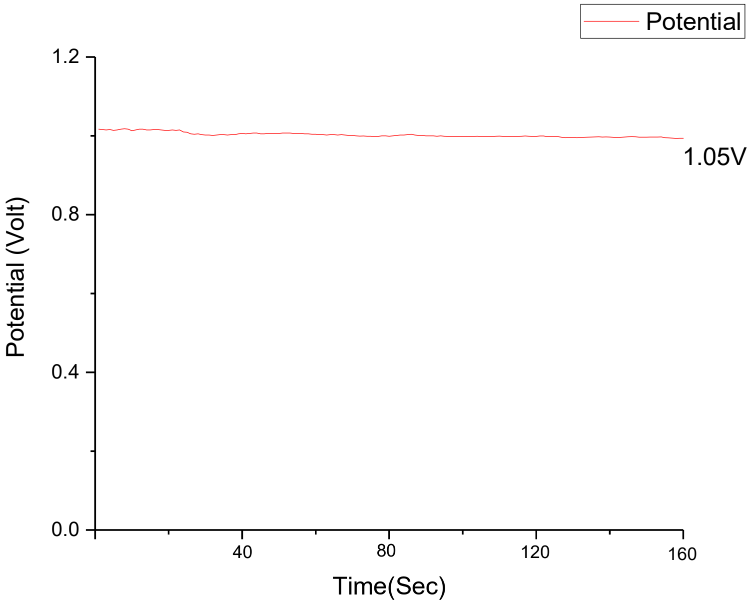

Fig. 4.12: OCPT Al-air battery (with bare PP)

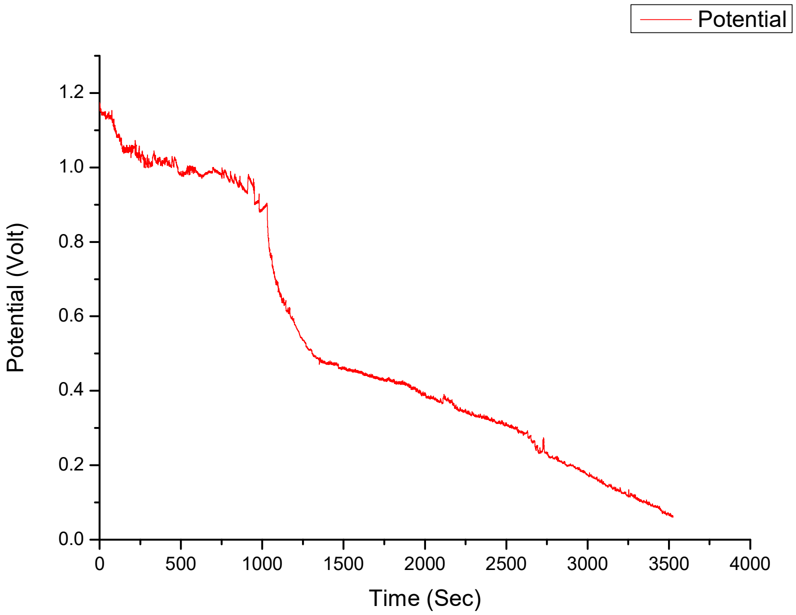

Fig. 4.13: Discharge cycle of Al-air battery

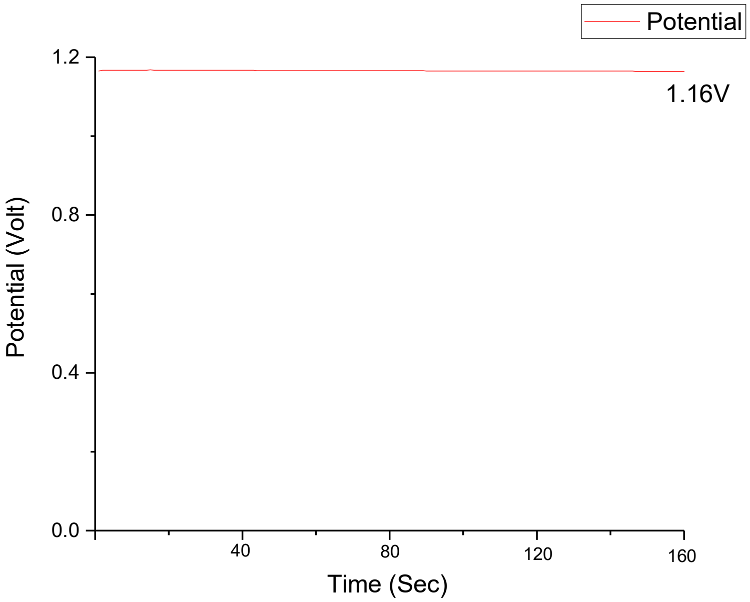

Fig. 4.14: OCPT Al-air battery (with SnO_2 coated PP)

OCP of Al-air battery made with SnO_2coated PP found to be comparable to that of bare PP Al-air battery.

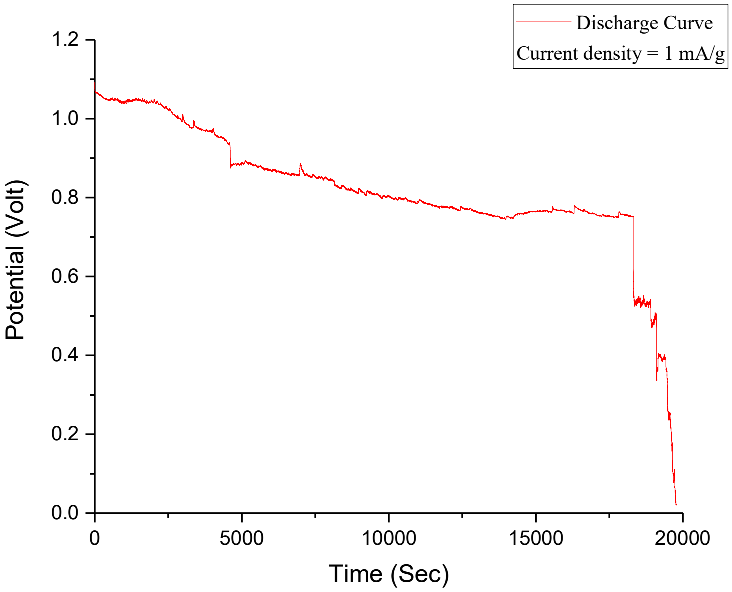

Fig. 4.15: Discharge cycle of Al-air battery (With SnO_2 coated PP)

Also the discharge time for Al-air battery with SnO_2 coated PP separator was found to be more than that of Al-air battery with bare PP separator. Also the discharge time was found to be more for Al-air battery with SnO_2 coated PP separator as compared to Al-air battery made using bare PP as stated in literature. [27]

EFFECT OF C RATE:

The C rate refers to how quickly a battery is charged or discharged in comparison to its maximum capacity. For example, 1C rate means the necessary current is applied or drained from the battery to completely charge or discharge it in one hour. We commonly use a C-rate of 0.1C in research which means battery takes 10 hrs to charge and discharge. Calculating the current necessary to charge or discharge a battery is easy as the capacity of battery is expressed in Ah (ampere-hour).It can be seen that at slow charge/discharge rates, plateaus along the potential plots are noticeable. Aluminium-ions intercalation and de-intercalation cause these plateaus occur at the redox potentials of the active materials. At higher C-rates such as 1C, the time required to completely intercalate and deintercalate the Al-ions is insufficient, resulting in a charge and discharge states mostly due to polarization of the battery. It can be seen that only a small percentage of nominal capacity is recovered.

4.5 Formation of SEI:

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 aluminium ion battery we study this SEI formation and found that after charge / discharge of battery this SEI is formed.

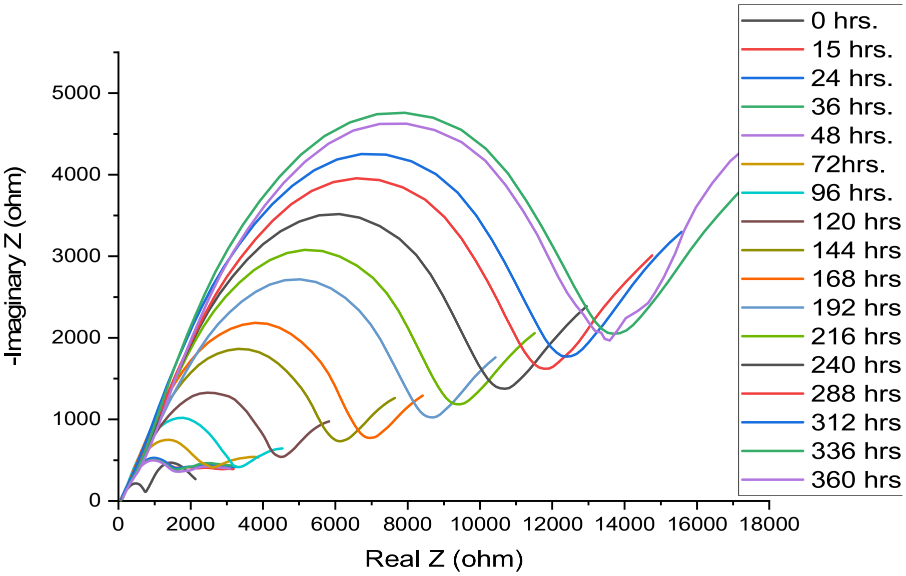

Fig 4.16 : EIS of Li symmetric cell with time

As from Table 4.2 and table 4.3 we can see that the capacity of battery is fading due to SEI formation which can be supported by performing EIS with time showing that impedance is increasing with time for Li symmetric cell prepared. Similar may be the reason for Al-ion battery so which is one of our future work plan.

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 two electron 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.

We can conclude that inspite of having many challenges to develop Al-ion battery solutions of it are being sought for it. Further development in this area will lead to a commercialization of this battery which is a promising option to Li-ion battery.

We are further working on this problem to improve the capacity by using various thin film deposition techniques used to deposite cathode material. Graphite 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. In future various oxides can be explored as coating material on separator and also aluminium alloys can be explored as anode material.

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