A NOVEL ALUMINIUM AIR RECHARGEABLE BATTERY WITH DEVELOPMENT IN ELECTRODE MATERIAL AND ELECTROLYTES.

M.Sc. Dissertation report by

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“A Novel Aluminium Air rechargeable battery with development in electrode material and electrolytes”

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To the

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April 2022

CERTIFICATE

This is to certify that the dissertation entitled **“A Novel Aluminium Air rechargeable battery with development in electrode material and electrolytes** “is Bonafide work carried out by Miss Beena Chauhan of M.Sc. (analytical chemistry) under my supervision in partial fulfilment of the requirement for the award of degree of Master of Science in Chemistry at School of chemical sciences , Goa University .

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ABSTRACT

The renewed interest in rechargeable Al-grounded battery chemistry is due to several interesting features. First, Al is inert and easy to handle in ambient atmosphere. Second, Al has the ability of swapping three redox electrons per cation and, thereby, it offers the pledge of enhanced energy storehouse than monovalent cations. Third, cost of Al minerals is fairly reasonable. Hence, the economics of deliverable energy (i.e., cost per kWh) from Al-batteries is anticipated to be appealing for consumers.

This review shows effect of materials, including Aluminium alloy and electrolyte type, in battery performance. Aluminium air batteries even though having advantage of high theoretical density has issues of (a) parasitic self -corrosion due to hydrogen gas evolution of aluminium at open circuit condition and under discharge. (b) Formation and Accumulation of hydroxides in alkaline environment.

The electrolytes studied were Gel polymer electrolyte ,solid electrolyte , Deep eutectic electrolyte .

For assessing the electrochemical behaviour of aluminium plot of open-circuit corrosion v/s discharge current needs to be studied.

With deep Eutectic solvent-grounded electrolyte battery capacity was observed to be lower than the theoretical value although stable electrochemical responses observed. When TiN was used as an air cathode material, by-products of the aluminium–air battery that is $Al(OH)_3$ and Al_2O_3 were not detected on either the Al anode nor the air cathode.

INTRODUCTION

Moment when the world is thriving to use day by day new technology everyplace , Electric Vehicles must be the future means of transport and thereby adding the use of renewable energy[1].

Because of fuel depletion , fluctuation in oil cost [2] and the air pollution arising from its combustion, there is an critical demand for renewable, clean fuel alternatives for our future energy supply[3]. Because of the constant increase in electrical demand of our society, new energy production, transport and storage systems will play a key role during a close to future[4] . Concerning to energy storage systems, electrochemical energy storage could be a terribly attention grabbing candidate due to only one step conversion of electrical energy to chemical energy and therefore the exhaust of typical energy resources and the ought to cut back greenhouse emissions and move towards a carbon emission [5] free economy. Advanced materials that let the economical harvest , storage, and utilization of renewable energy are at the center of current analysis within the energy field [6] .To date, Lithium [7] ion batteries are the foremost fortunate energy-storage solution; they need been wide utilized in each portable electronic devices and electrical vehicles (EVs) since the primary report was created on them in 1991 [4]. the battery is desired to be safer, offer longer life, temperature resistance, and low cost[8].

In the past decade, there have been exciting developments within the field of lithium-ion [9] batteries as energy storage devices, leading to the appliance of lithium-ion batteries in areas starting from small transportable electrical devices to massive power systems like hybrid electrical vehicles. However, the maximum energy density of current atomic number particle batteries having topotactic chemistry isn't suffient to meet the stress of latest market in areas as electrical vehicles [2] a pair of and deficiency and price of lithium resources set additional attentions towards searching into different metals as alternatives for Li-based batteries. Zinc, aluminium, sodium, magnesium, as additional metals, may function as such alternatives [10].Therefore , metal -air batteries like Aluminium metal that is abundantly available in India are thought of a promising candidate [2] in replacing Lithium batteries .Since Aluminium[11] (Al)/air batteries have the potential to be wont to manufacture power to control cars and different vehicles. The Al/air battery system can generate enough energy and power for driving ranges and acceleration almost like gasoline powered cars [12]

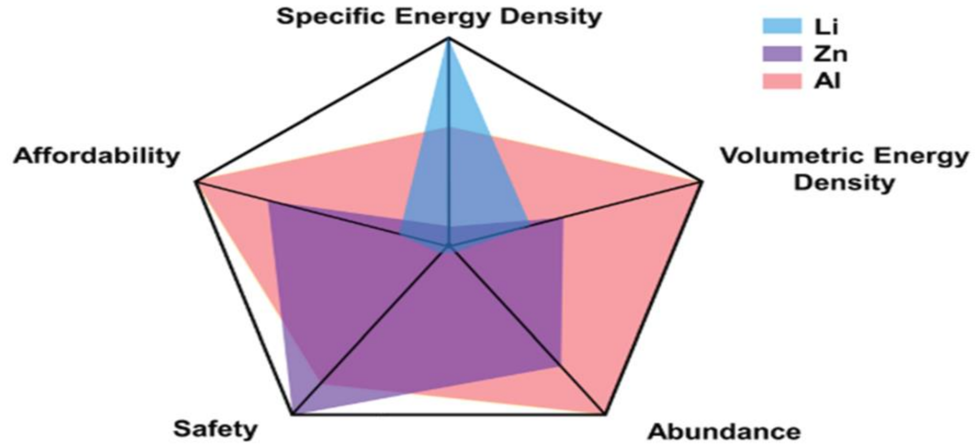


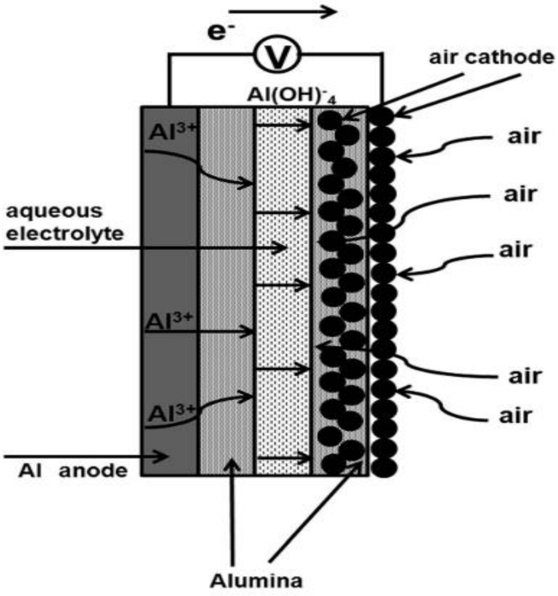
Fig. 2 Comparisons of Li, Zn, Al-based MABs in terms of the specific energy density, affordability, safety, abundance, and volumetric energy density.

Above Figure shows comparisons of specific energy density of different metal air batteries [13].

Al/air battery system features a high theoretical voltage (2.7 V), high theoretical energy density (8.1 kWh/kg-Al), low cost, surrounding friendly ,eliminate carbon dioxide [14] emission and recyclable product and therefore the advantage is light -weight of batteries because of use of atmosphere element (oxygen) as fuel and therefore it seems to be a promising system for EVs [12] . Meanwhile, aluminium (Al) is cheap , safe, and is the third most abundant element in the Earth's crust [6]. The aluminium/air battery has advantages of the lower price and higher theoretical energy density[15] .

Basic elements of aluminium-air battery

Air Cathode: composed of Conductive carbon and Polyvinylidene difluoride (PVDF) in N-methyl – pyrrolidine taken in proper proportion of 2:1:7 to the electrodes. Al_2O_3 Lid where powder mixed in proportion 8:1:1 Al_2O_3: carbon: PVDF , Al_2O_3 film , metal manufactured from Aluminium board, 10% NaCl aqueous solution was utilised in studies as Electrolyte[3] .



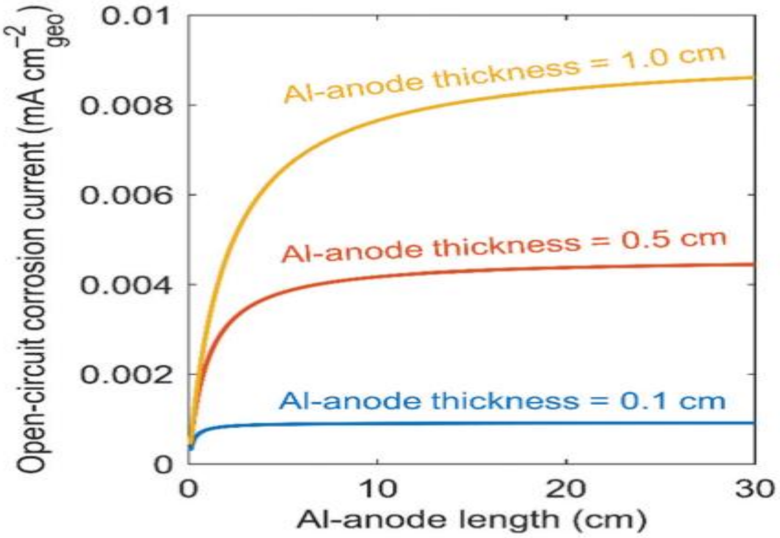
Aluminium -air rechargeable battery was studied by utilising Al_2O_3 as buffer to supress by product formation directly onto an Aluminium anode and air cathode. However aqueous electrolyte want to be endlessly fed that created a issue . The metal air battery needs better electrolyte and better anode material .

Evaluating electrochemical behaviour of aluminium

To evaluate the corrosion[16] behaviour of Aluminium metal the quantitative technique is employed , which involves measurement of corrosion current as a function of applied potential or discharge current .

The measurements of open-circuit corrosion current rely on multiple variables like temperature, total electrolyte volume, whether or not the electrolyte solution is flowing or static, and the amount of Al that's already dissolved within the electrolyte. The corrosion current will increase with increase in length and thickness of metal anode.

Corrosion current of Aluminium is beyond **1 mACm-²**.

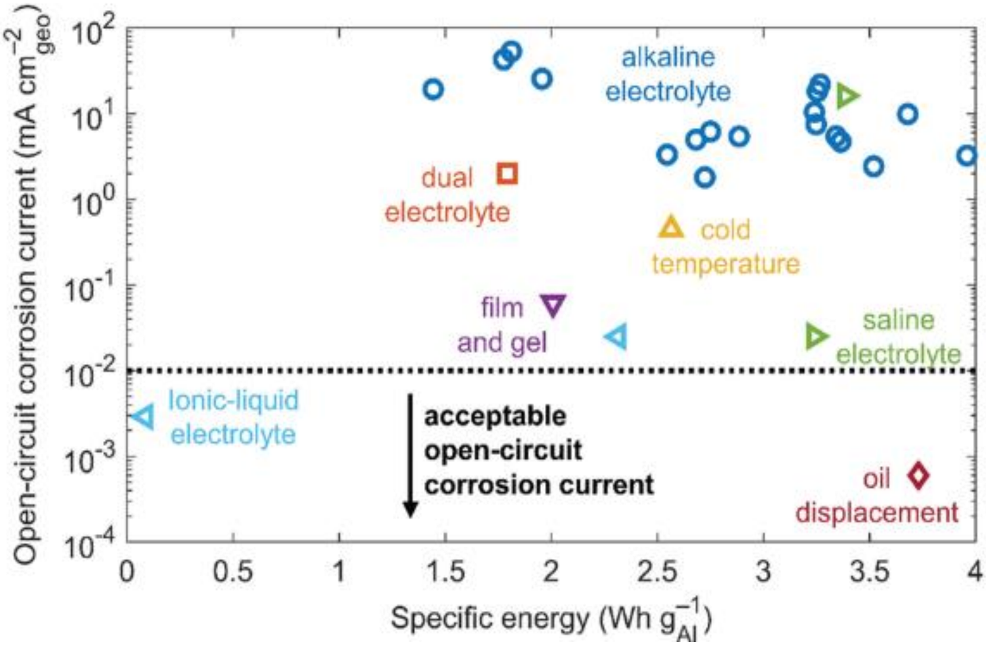


Different corrosion mitigation strategies[17] involves anode alloying , electrolyte additives, saline electrolytes, ionic-liquid electrolytes, dual electrolytes, gel electrolytes, anode films, cold temperatures, anode grain sizes.

The studies show that with increase in Al anode length the electric /open circuit corrosion current will increase.

From above plot of electric circuit corrosion v/s Al-anode length it's clear that , lower the open circuit corrosion , lower the specific energy. Thicker and larger Aluminium anode greater the acceptable corrosion. Ionic liquid electrolytes induce low corrosion current however conjointly it provides low specific energy density, since ionic liquid electrolytes have low water intake thereby reducing the corrosion .

Aluminium–air cells utilising oil displacement systems, reach the lowest corrosion current with high specific energy , they use alkaline electrolyte solution throughout discharge then again displace this electrolyte with oil once the battery isn't in use. A tiny low portion of electrolyte dissolves within the displacing oil, yielding a low open-circuit corrosion current and little corrosion still continuous. saline electrolytes conjointly provide with high specific energy .



Choice of electrolyte for Aluminium-air cells

The different variety of electrolytes used for metal-air batteries are solid electrolytes ,Gel polymer electrolyte[13] , hybrid electrolytes [7], deep eutectic solvent based electrolyte[18] .

Solid -State Electrolyte:

Scientists, Yuantao ,Yuchuan ,Chen, Xiao *a and Shujiang Ding *ac[13] studied the improvement in solid electrolytes in Al– air batteries .This analysis is concerning development in solid electrolyte utilised in aluminium batteries , traditional Flowing Electrolyte is replaced by solid electrolyte. There are two type of Alkaline solid electrolyte found , Alkaline anion exchange membrane (AAEMs) and Gel Polymer electrolyte (GPEs) .Framework material used for solid electrolyte battery were artificial organic polymer ,biomass material and inorganic material .

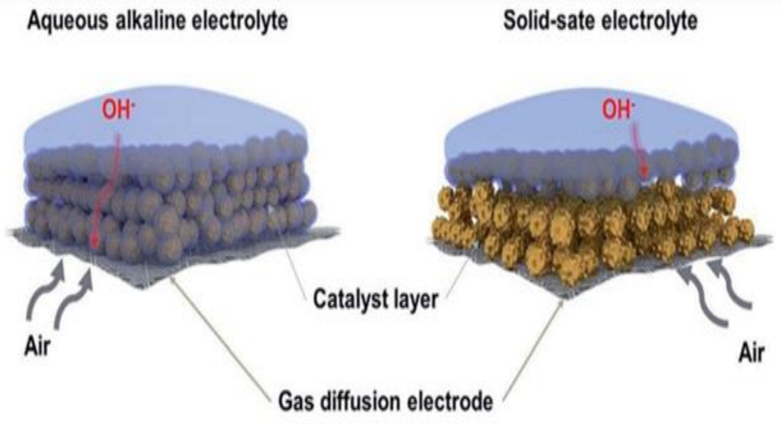
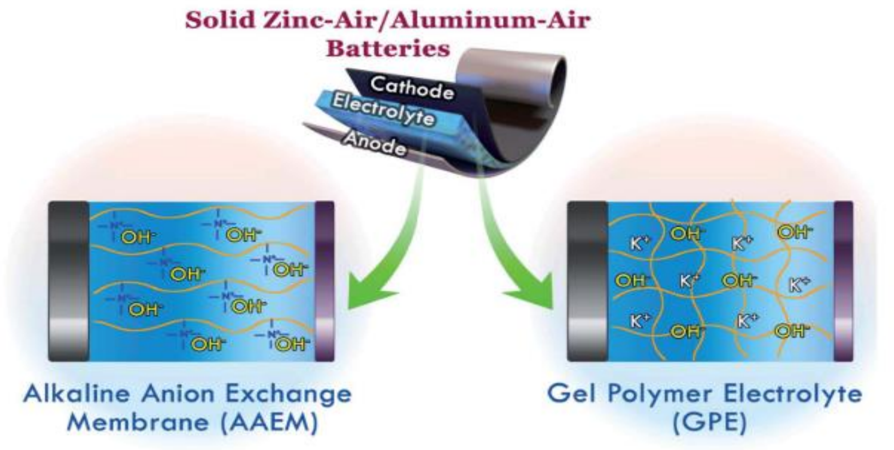


Fig. 21 Demonstration of the three-phase reaction regions using aqueous and solid electrolytes. Reproduced with permission.[16] Copyright 2016, Wiley-VCH.

Gel polymer electrolyte have higher conductivity (10-^{1} Scm-^{1}) far as compared to Alkaline anion exchange membrane (10^{-3} to 10^{-2} Scm^{-1}).

Ionic conductivity plays awfully necessary role within the electrochemical performance of flexible batteries. The conductivity of the alkaline GPE (10^{-1} Scm^{-1}) is far a lot of that of the organic GPE and the all-solid-state electrolytes (10^{-7} to 10-^{3} Scm-^{1}), there is still a large gap particularly for the aqueous electrolyte, especially for AAEMs (10^{-3} to 10-2 Scm$^{-1)}$ with its rigid skeleton structure, like the benzene ring and imidazole. The foremost direct approach is to manage the OH$^-$ content within the membrane, but too high of an alkali concentration can destroy the membrane structure and increase the viscosity, thus spoiling conductivity. Straightforward treatments, like introducing other hydrophilic materials, adding fillers, fabricating porous structures, and grafting hydrophilic groups, can rapidly increase the conductivity.

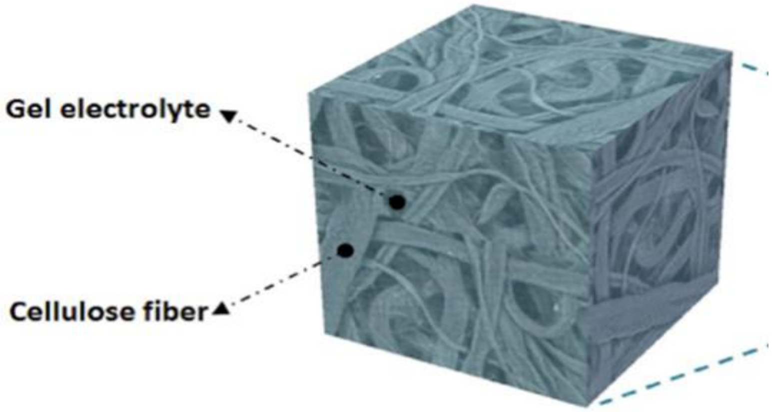
Again the difficulty of ion movement is related to mechanical strength and which ends in decrease in conductivity. The mechanical strength can be multiplied by either cross linking, Chemical cross-linkage with little molecules could be very effective method to enhance the interaction between polymer chains, and building an interpenetrating polymer network or a dual-network system, or adding support materials[13].



Schematic diagram of the two solid electrolytes: AAEM (left) and GPE (right).

<u>Paper – based Gel Electrolyte</u> :

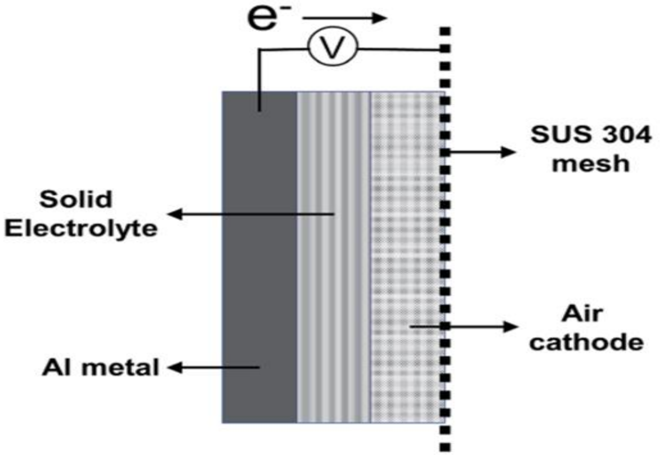
The paper-based [19] gel electrolyte is developed for liquid-free Al-air batteries, that is principally being used for small-power transportable electronic devices. Cellulose paper is utilized as a porous skeleton to store the alkaline gel, leading to a flexible, ultrathin and degradable product. To minimise leakage hazard, aqueous alkaline electrolyte has been coagulated (solidified) into a gel electrolyte, that is usually accomplished by adding a gelling agent into the alkaline solution. Such a gelling agent includes poly (vinyl alcohol) (PVA), polyacrylic acid (PAA), poly (ethylene oxide) (PEO), etc. Once utilised during a mechanical-rechargeable Al- air battery, the electrolyte and therefore Al anode are replaceable after exhaustion, so that the battery may be used for multiple times.



Deep Eutectic Solvent based electrolyte :

In some analysis study Deep eutectic solvent based electrolyte are used conjointly been used in order to create rechargeable battery , Also it has been found by scientist Ryohei Mori * [18] that deep eutectic solvent based electrolyte exhibit rechargeable behaviour and a value advantage over ionic liquid-based electrolytes. When a aluminium air battery need to be created it important that it is in a tough form so that it can be easily used and should be easy to manufacture which can result in further lead to reducing the price of battery .

Ionic based electrolyte gets evaporated easily, hence deep eutectic solvent [6] based electrolyte are safer and better . During this study $AlCl_3$, urea, carboxymethyl cellulose (CMC), and glycerine was used as electrolyte and, titanium nitride (Tin) and polyvinylidene difluoride (PVDF) was used as Air cathode material and aluminum board used as anode .



Schematic figure of Al–air battery prepared in this study.

Chloroaluminate melts are well known for their high affinity to aluminum electrodeposition and have been thought of as attainable electrolytes for the improvement of secondary Al ion batteries.

In basic medium each $AlCl_4^-$ and Cl^- species coexist whereas in neutral melts, the only anionic species is $AlCl_4^-$. In acidic melts, the predominant species is $Al_2Cl_7^-$.

The charge -discharge curve showed that though the capacity was smaller than the theoretical value, it absolutely was stable even after a large number of charge–discharge electrochemical reactions.

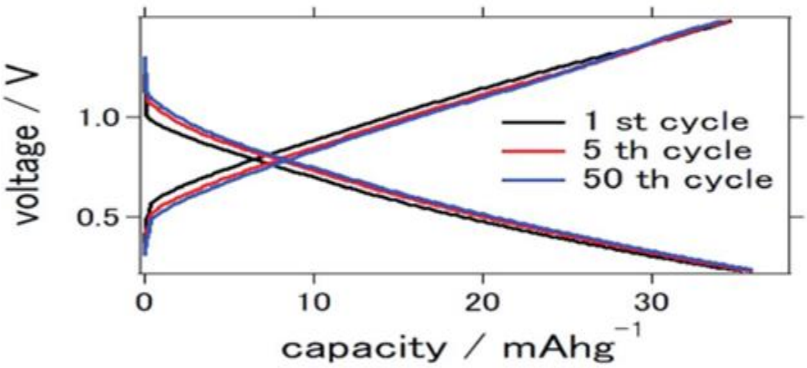


Fig. 2 Charge–discharge curves of the all solid state Al–air battery with TiN air cathode prepared in this study.

CMC was acting as a viscosity thickener to prepare a solidified electrolyte and glycerin was used as humectant that reduces the volatility of electrolyte .

The study of deep eutectic[18] solvent based electrolyte conjointly showed that by-product formation of $Al(OH)_3$ and Al_2O_3 was suppressed .Excellent catalyst for oxygen reduction are metal nitride and carbide .

In some research paper , a light-weight, ultrathin and flexible paper-based gel electrolyte[19] has been developed for liquid-free Al-air batteries, which uses a natural cellulose paper to store an alkaline gel.

Reaction taking place in cell are:

As shown by the following equations, the major reactions occurred in Al-air battery include Al oxidation in the anode (Eq. (1)), oxygen reduction in the cathode (Eq. (2)), the overall reaction (Eq. (3)) and the side reaction of Al corrosion (Eq. (4))

$$\text{Anode: } Al + 3OH^{-} \rightarrow Al(OH)_3 + 3e^{-} \tag{1}$$

$$\text{Cathode: } O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-} \tag{2}$$

$$\text{Overall: } 4Al + 3O_2 + 6H_2O \rightarrow 4Al(OH)_3 \tag{3}$$

$$\text{Al corrosion: } Al + OH^{-} + 3H_2O \rightarrow Al(OH)_4^{-} + \frac{3}{2}H_2 \tag{4}$$

Effects of Cations in ionic Liquid electrolytes

Room temperature ionic liquids (RTILs) are solvent free liquids comprised of densely packed cations and anions. Ionic liquids have low vapour pressure and low flammability making Ionic liquid electrolytes better candidate for electrolytes. In this paper [20] rechargeable aluminium/graphite battery electrolytes was studied by mixing 1-methyl-1-propylpyrrolidinium chloride (Py13Cl) with various ratios of aluminium chloride ($AlCl_3$).

Fundamental property of Ionic Liquid was studied like density, viscosity, conductivity, anion concentration and electrolyte ion percent. This properties of Py13Cl with $AlCl_3$ were compared with previously developed 1-ethyl -3- methylimidazolium chloride (EMIC -$AlCl_3$)

Py13- Cl-$AlCl_3$ Ionic liquid showed low density, higher viscosity and lower conductivity than EMIC-$AlCl_3$.

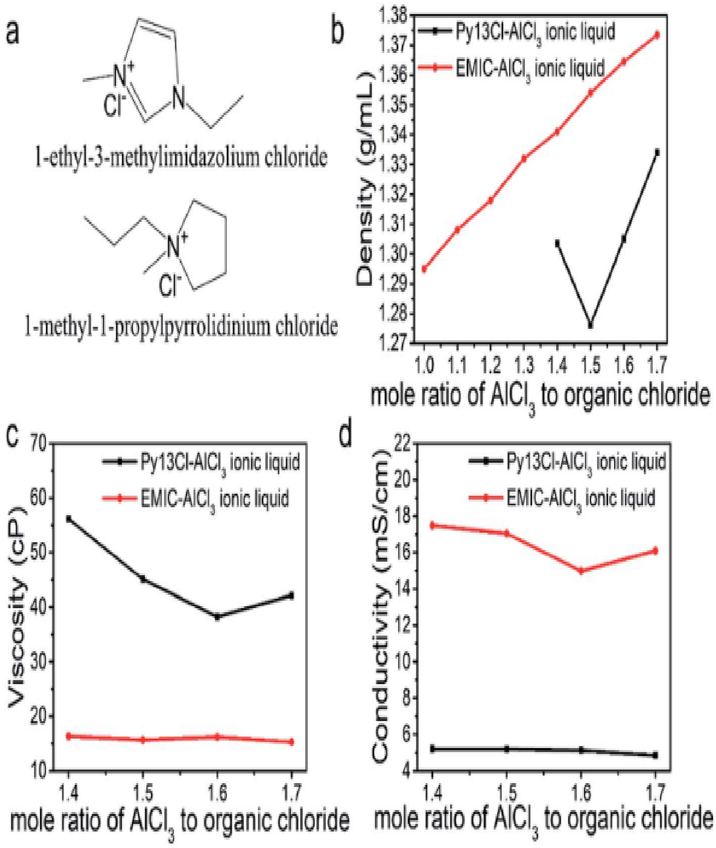


Fig. 1 Structures and physical properties of Py13Cl–$AlCl_3$ and EMIC-$AlCl_3$ ionic liquid. (a) The structure of EMIC and Py13Cl, (b) density comparison between Py13Cl–$AlCl_3$ and EMIC-$AlCl_3$, (c) viscosity comparison between Py13Cl–$AlCl_3$ and EMIC-$AlCl_3$ measured at 23–24 °C. (d) Conductivity comparison between Py13Cl–$AlCl_3$ and EMIC-$AlCl_3$ measured at 25 °C.

Larger (AlCl3) n species were found in Py13Cl-AlCl3 system and showed larger overpotential as compared to EMIC-AlCl3, hence giving lower energy efficiency and low conductivity .

When the cation size changes in an ionic liquid, it might greatly have an effect on the chemical environment around it and its solvation shell. Bigger size cations could stabilize and favour the formation of larger species such as (AlCl3)n . In addition, the pi- system and the Brønsted acidic set of hydrogen atoms, which were unique in the EMI+ and absent in the Py13+, helped with solubilizing and liquidizing of the ionic liquid. Larger (AlCl3)n species tend to form in the Py13Cl–AlCl3 system , Larger (AlCl3)n species were only observed in Py13Cl–AlCl3 ionic liquid . Hence smaller cations could have positive effects on

the battery, by decreasing the viscosity and increasing the conductivity of the resulting electrolyte. This could provide a guide to the synthesis of new ionic liquids for optimized batteries within the future.

Use of electrolyte Additives :

Dithiothreitol and Butantetraol :

Some research papers have conjointly reported use of Dithiothreitol [15] additive for alkaline Aluminium batteries .Dithiothreitol (DTT) is considered as a green additive for Aluminium air batteries .The aluminium-air battery produces electricity from the reaction of oxygen in the air with aluminium . Due to self-corrosion (due to hydrogen gas evolution) it results in reduction in energy efficiency since in alkaline medium insoluble oxide is formed. Therefore an additive like Dithiothreitol a green additive is used to retard self-corrosion of Al-anode.

Dithiothreitol has a stronger ability to increase the discharge capacity than butantetraol. The improvement was done by suppressing of the side reaction of hydrogen evolution. DTT has better protection effect than BTT, the dynamic covalent bond of thiol- disulphide exchange provides intelligent inhibition for hydrogen evolution reaction. It is seen that dithiothreitol can form a uniform and stable protective layer through dynamic covalent bonds on aluminium anode surface. DTT can absorb on aluminium surface to form a stable complex. The –SH groups in DTT is beneficial to form a six-membered ring complex, increasing the coverage on aluminium surface. DTT is a promising additive used to drive the practical application of aluminium/air battery.

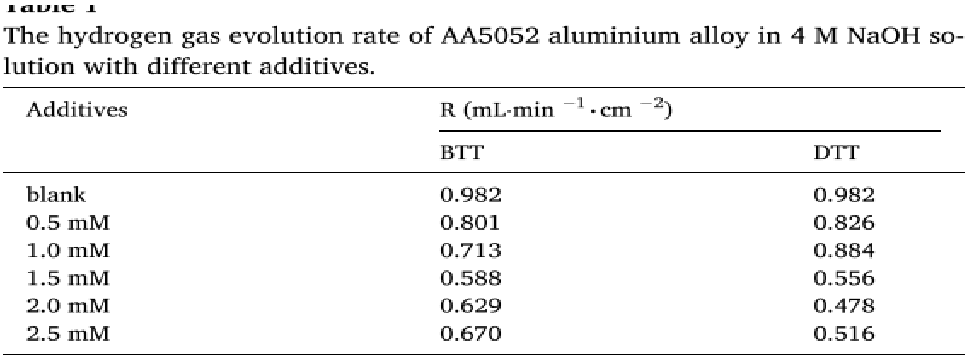
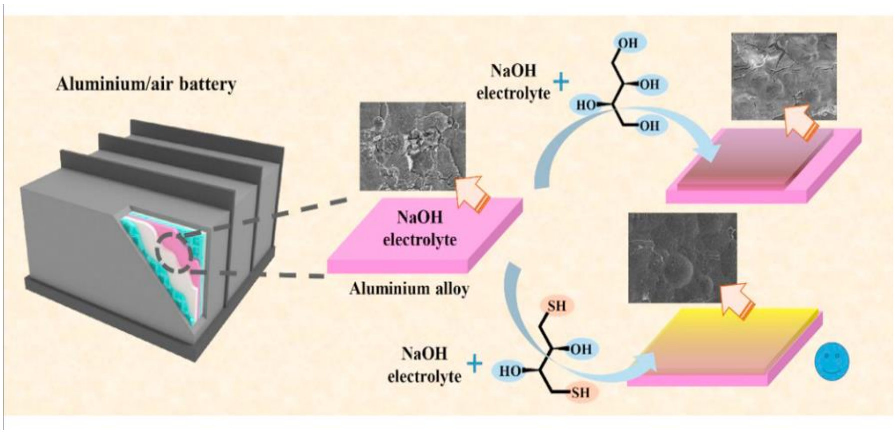


Table 1

The hydrogen gas evolution rate of AA5052 aluminium alloy in 4 M NaOH solution with different additives.

Additives	R ($mL \cdot min^{-1} \cdot cm^{-2}$)	
	BTT	DTT
blank	0.982	0.982
0.5 mM	0.801	0.826
1.0 mM	0.713	0.884
1.5 mM	0.588	0.556
2.0 mM	0.629	0.478
2.5 mM	0.670	0.516

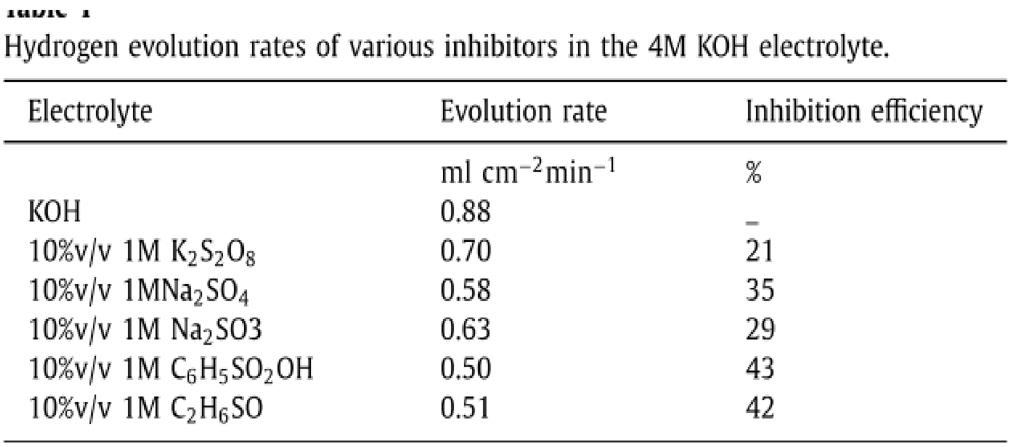
From above studies it is clear that DTT retards the hydrogen gas evolution which leads to corrosion .



Use of SO- group [10] as additives for improving rechargeable Aluminium air batteries, to retard corrosion of aluminium anode .Inorganic and organic additives have been used , the performance of organic and inorganic additives were compared . The role of additive is to reduce rate of undesired reactions , increase anode utilisation ,enhance discharge capacity ,and improve life cycle of battery . Additives used were inorganic ,organic ,polymers ,ionic liquid ,hybrid electrolytes .

Additives used were Na_2SO_4, Na_2SO_3, C_2H_6SO, $C_6H_5SO_2OH$ with discharge capacity of 2604,2393,2348, and 2048 mAg^{-1}

Hydrogen evolution rate with C_2H_6SO additive was observed to be the least and inhibition efficiency was 42% (highest).



Hydrogen evolution rates of various inhibitors in the 4M KOH electrolyte.

Electrolyte	Evolution rate	Inhibition efficiency
	ml cm^{-2}min^{-1}	%
KOH	0.88	–
10%v/v 1M $K_2S_2O_8$	0.70	21
10%v/v 1MNa_2SO_4	0.58	35
10%v/v 1M Na_2SO3	0.63	29
10%v/v 1M $C_6H_5SO_2OH$	0.50	43
10%v/v 1M C_2H_6SO	0.51	42

The studied additives help to slow down the unfavourable self- corrosion process.

Acetoxy based additives

In this study acetoxy[21] based group were used as additives for protecting anode of rechargeable air battery . The inhibitors have been acting as barriers on the anode's surface to mitigate metal corrosion.

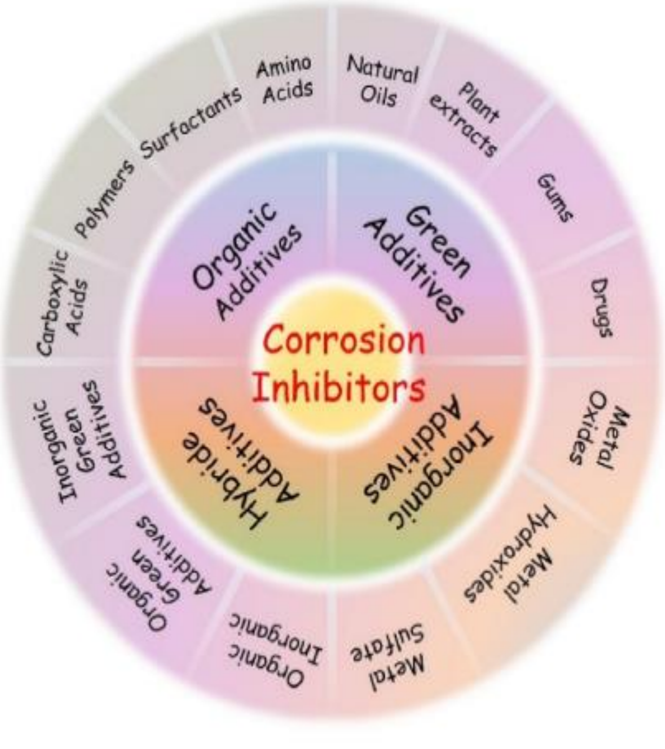
Various inhibitors used are zinc oxide, sodium oxide and sodium stannate and cerium nitrate.

Zinc oxide forms porous and loose film layer on Aluminium anode used in hybrid electrolytes.

Inorganic inhibitors are able to activate the passivated layer of anode and form a protecting film on the anode's surface which helps to suppress self-corrosion.

Tetra butyl ammonium fluoride, carboxylic acid ,8-hydroxyquinoline, nonoxynol - 9 have lower performance since it is a organic additives, but give improved inhibition efficiency.

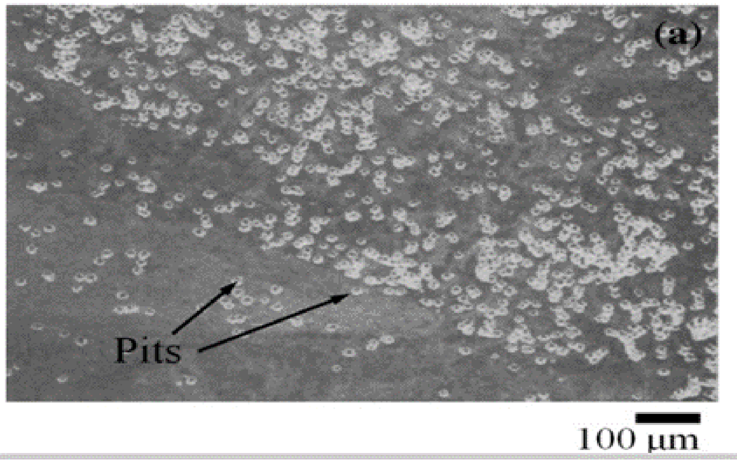
Hybrid electrolytes such as alkyl polyglucoside/potassium stannate, L-aspartic/metal oxide, sodium stannate/ casein, cerium/praseodymium mercaptoacetate, carboxymethyl cellulose/ ZnO ,8-hydroxyquinoline/ZnO and poly (ethylene glycol)/ZnO, have effectively retarded the self-corrosion of Al in alkaline electrolytes.



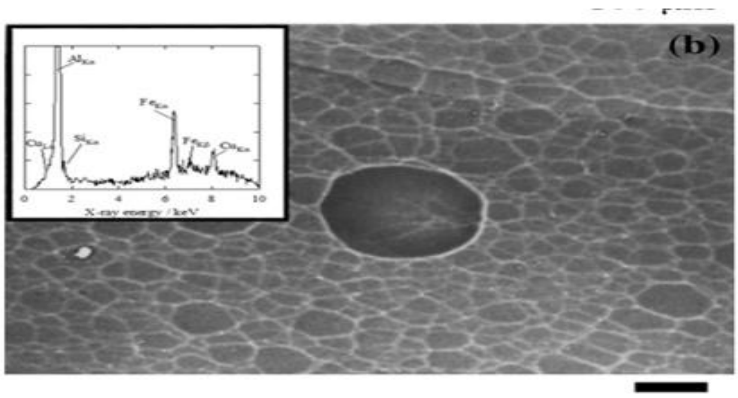
Scheme 1 – Various types of inhibitors in Al corrosior

The influence of alloying elements :

Development in the electrode material and electrolytes [16] was done to overcome the corrosion of aluminium at open-circuit potential since there is reduction of water on anode and formation of a passive hydroxide layer on aluminium. Using alloys for aluminium air batteries, which includes Mg, Zn, Pb, Sn, Ga, In, these elements are used as a they have lower melting temperatures than aluminium and inhibit corrosion.



SEM image of Al/0.05 Ga alloy



Back scatter electron image of 99.999% Al discharge

Also, we could use anionic membranes and gel electrolytes or alternative solvents which would include alcohols or ionic liquids, to replace aqueous solutions is another method to reduce corrosion.

Effective alloying element should have been possessing the following properties: (i) a melting point below the melting temperature of aluminium (657 deg.C), (ii) good solid solubility in the aluminium matrix, (iii) a higher nobility than aluminium, good solubility in an alkaline electrolyte.

To facilitate alloy diffusion in the aluminium matrix via solution heat treatment to form a solid solution alloy, the melting temperature of the alloying element should be lower than that of pure aluminium

When alloying elements are in solid solution with the aluminium matrix, yielding higher anodic currents the alloy will activate the aluminium.

The alloying elements should be more noble than aluminium since this is mechanism by which the alloying element activates aluminium in alkaline solutions.

Plant extracts[16] are also considered as corrosion inhibitor which ca replace the toxic chemicals

Use of metal - Organic framework (MOF) :

Use of metal organic framework [22] as air cathode ,aluminium terephthalate (AT) has been used as a metal–organic framework (MOF) material for the air cathode and 1-ethyl-3-methylimidazolium chloride as an ionic liquid electrolyte for development of rechargeable aluminium–air battery , thereby providing high capacity and long- term durability in charge–discharge electrochemical reactions.

Charge discharge curves of the aluminium–air battery using activated carbon (AC) , aluminium terephthalate (AT) (as MOF material only), and AT with conductive carbon (ATCC) for the air cathode.

These studies showed that cell capacity was lower at the first cycle, its value after 25 cycles remained almost the same when we used AT as the material for the air cathode. These studies confirmed that the use of AT as MOF for the air cathode resulted in high durability of the aluminium–air battery system in repetitive charge–discharge electrochemical reactions. The formation of Al $(OH)_3$ and Al_2O_3 on the anode electrodes, which are being considered as by products are inhibited on anode .

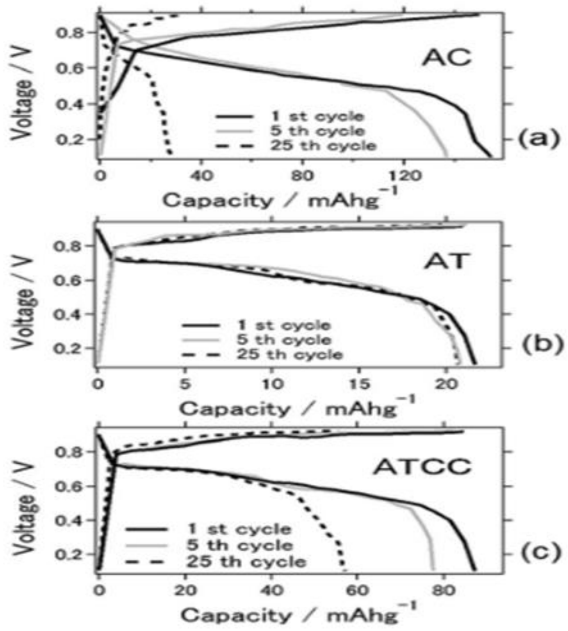


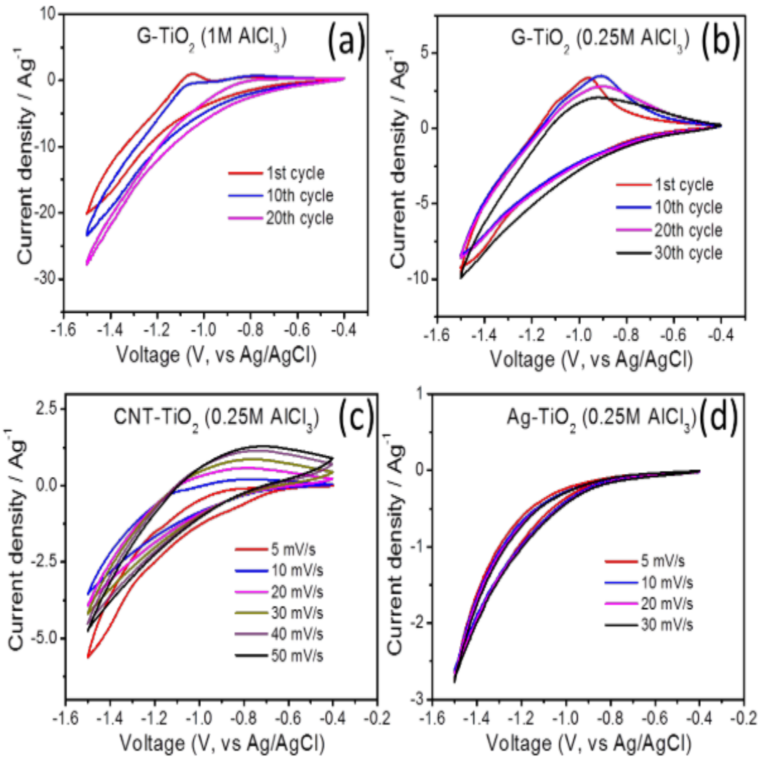
Fig. 2 Charge–discharge curves for the aluminum–air battery with the air-cathode materials (a) AC (b) AT and (c) ATCC.

Anode material for Aluminium ion batteries :

Anatase TiO_2[11] as an Anode Material for Rechargeable Aqueous Aluminium-ion Batteries is studied.

electrochemical intercalation and extraction of Al^{3+} ion in anatase TiO_2 in aqueous electrolyte is studied. TiO_2 gives poor electronic conductivity due to poor diffusion of Al^{3+} , this is improved by adding graphene .Graphene induces ultrafast diffusion of Al^{3+} ion in TiO_2.

To understand the Al^{3+} ion insertion mechanism, CV was performed at different scan rates



Cyclic Voltammetry is an electrochemical technique which measures the current that develops in a electrochemical cell under conditions where voltage is in excess of that predicted by Nernst equation

Also used to study presence of intermediate in oxidation -reduction reaction and reaction mechanism.

Characterisation of Aluminium surface :

Surface analysis done by SEM [10] technique aluminium's surface after 2 hours of immersion in (a) KOH, (b) $K_2S_2O_8$ /KOH, (c) Na_2SO_4 /KOH, (d) Na_2SO_3 /KOH, (e) $C_6H_5SO_2OH$/KOH, (f) C_2H_6SO/KOH

S. Hosseini, Z.-Y. Liu, C.-T. Chuan et al. Electrochimica Acta 375 (2021) 137995

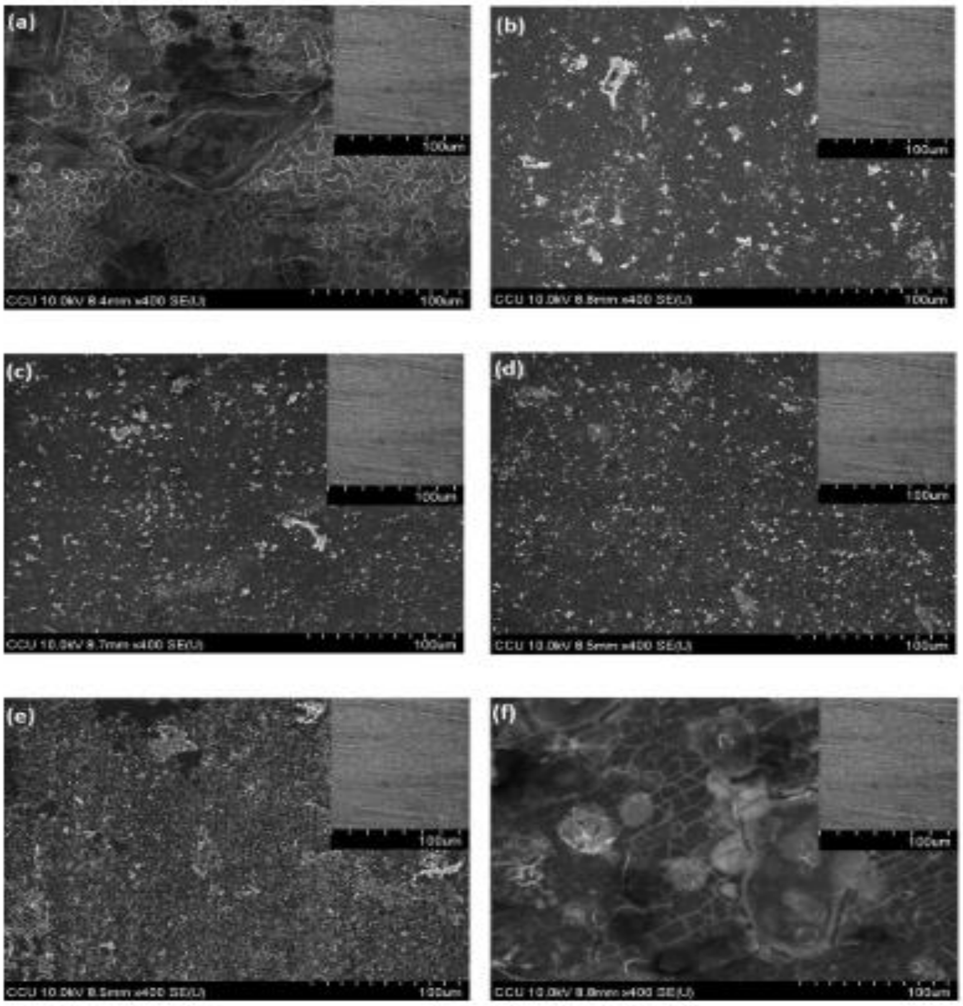


Fig. 3. SEM images of the aluminium's surface after 2 hours of immersion in (a) KOH, (b) $K_2S_2O_8$/KOH, (c) Na_2SO_4/KOH, (d) Na_2SO_3/KOH, (e) $C_6H_5SO_2OH$/KOH, (f)

(a) When Aluminium immersed in the KOH solution, resulting in the formation of pits and cracks. The Crater- like micro-features with grooves are clearly seen after a 30-min immersion.

(b) shows the formed micro structured pits with white precipitates when KOH/$K_2S_2O_8$ is used.

(c) with less corrosion pits are observed with both KOH/Na_2SO_4 and KOH/Na_2SO_3 .This proves that additives can inhibit corrosion.

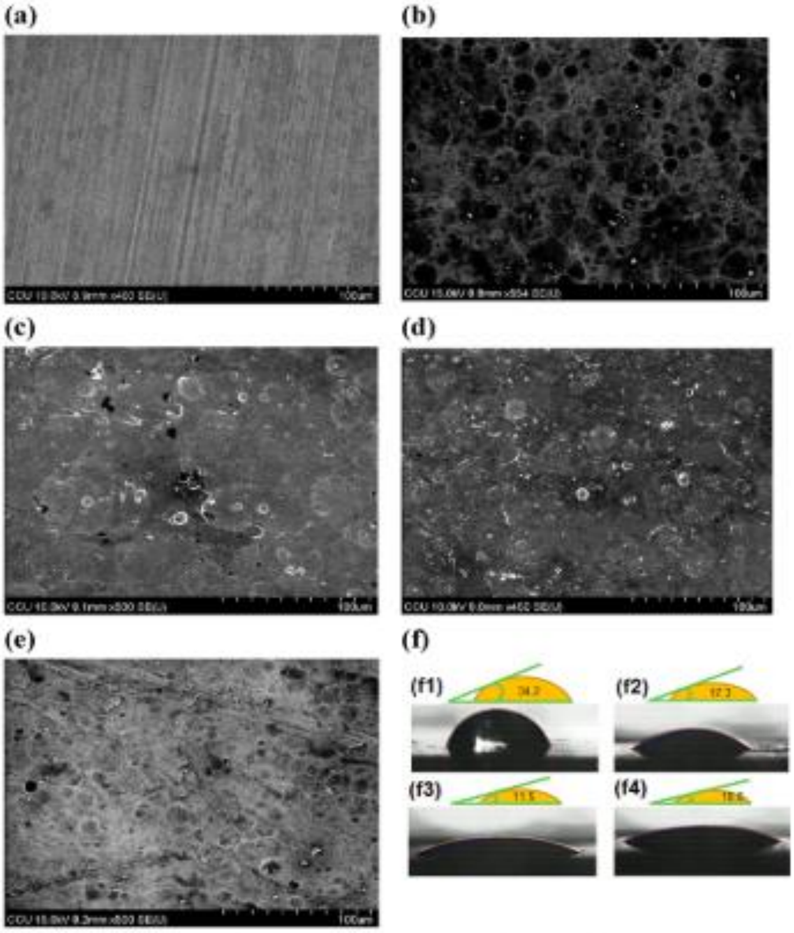


Fig. 4 – SEM images of the aluminium's surface (a) without electrolyte (pristine), after 2 h exposed in (b) KOH, (c) eth KOH, (d) Ba-AC/KOH, (e) Ca-AC/KOH and (f) Schematic of the contact angle for four electrolytes (f_1) KOH, (f_2) ethyl-Ac/KC Ca–Ac/KOH and (f_4) Ba–Ac/KOH on the Al's surface.

SEM images [21] of the aluminium's surface (a) without electrolyte (pristine), after 2 h exposed in

(b) KOH, (c) ethyl-Ac/ KOH, (d) Ba-AC/KOH, (e) Ca-AC/KOH

(a) shows a plan uniform surface (b) shows uneven and non uniform surface

(c) shows the pits with small cracks appearing on the surface of Al when Ca- Ac/KOH electrolyte is used.

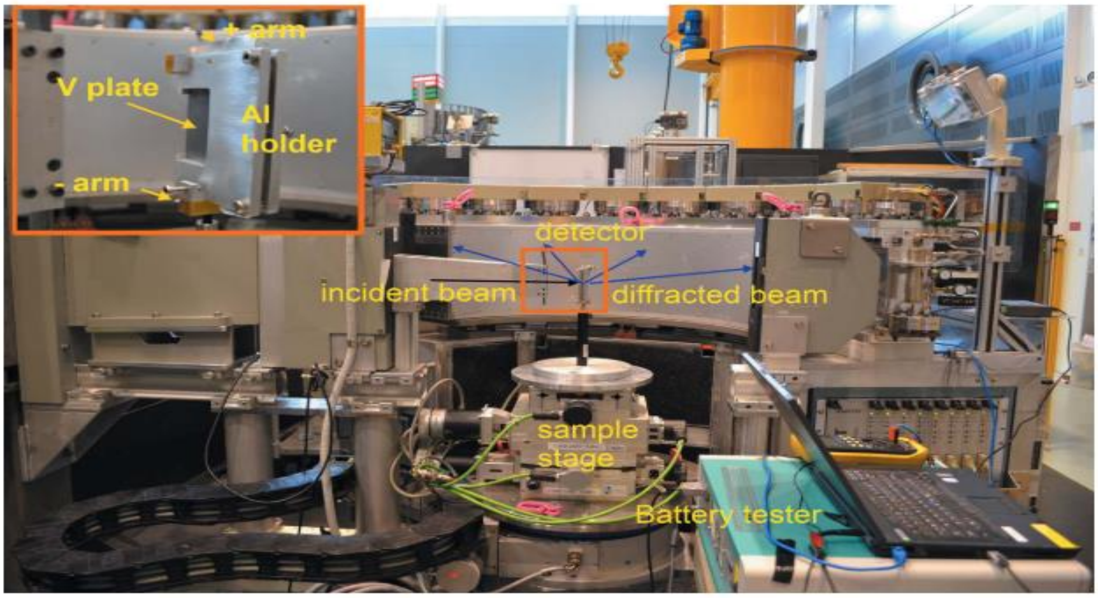
(d)The surface of the aluminium in the presence of Ba-Ac/KOH has minor etched pits

(e) the corrosion has been better inhibited compared to the Ca-AC/KOH and ethyl-Ac/KOH cases

With addition of additives adsorbed on the Al's surface forms a protective layer, ,which in turn will help to prevent water reduction reactions and hydrogen generation.

Study of electrode structure :

The rechargeable air batteries performance is governed by structural and phase changes during cycling. Neutron Powder diffractilon (NPD) [23] provides unique and useful information concerning the structure function relation of battery components. For the measurement of the phase and crystal structure evolution[23] of active materials within batteries during cycling NPD is a valuable technique .



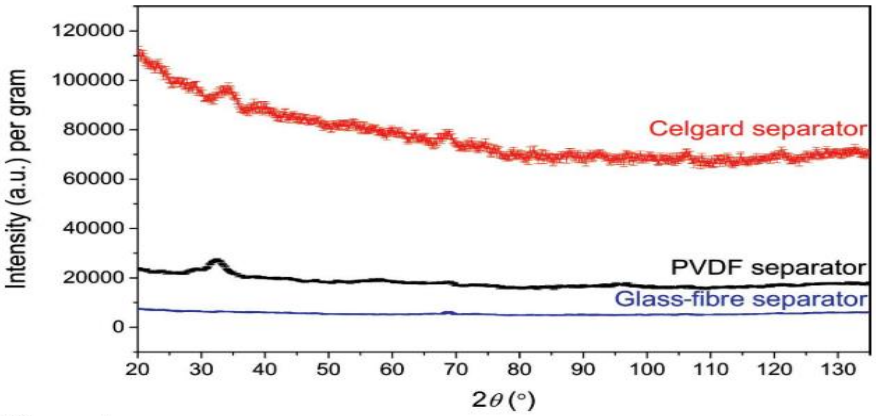
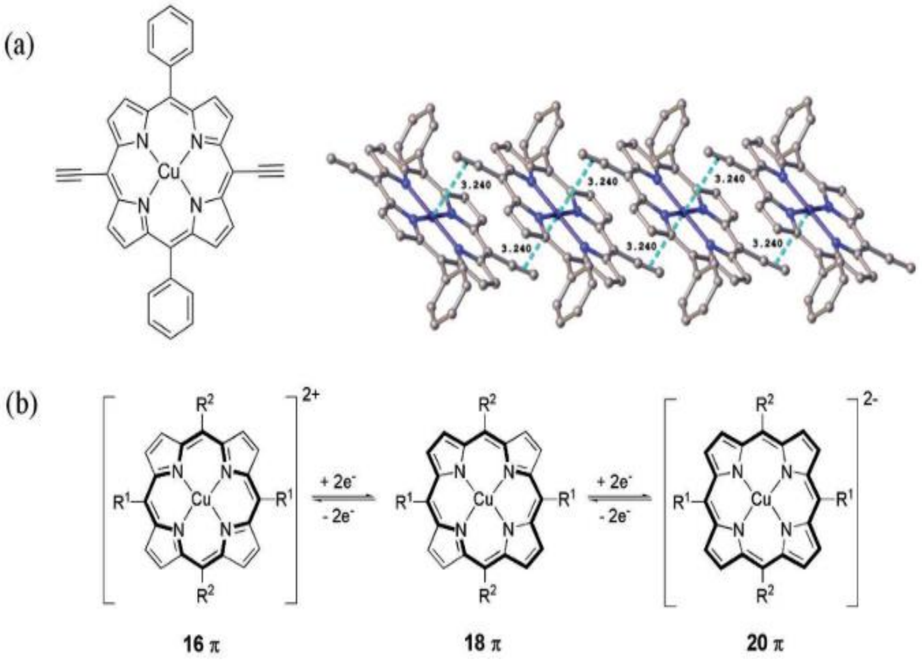


Figure 4
NPD patterns of polypropylene (Celgard), polyvinylidene difluoride (PVDF) and glass-fibre separators.

Use of organic material for energy storage device:

Organic energy storage materials[24] are also considered as future candidate for electrochemical energy storage . Organic materials are attractive due to their low cost, recyclability, resource sustainability environmental friendliness, structural diversity, and flexibility. Novel Porphyrin based electrode material might replace both anode and cathode in rechargeable Li-ion batteries

Porphyrin-based active materials have drawn great interest as new class of organic electrodes porphyrin-derived synthesis strategies help in modifying the structure and composition of organic electrode and thereby increasing conductivity in energy storage devices.



a) Chemical and crystal structure of CuDEPP complex [5,15-bis- (ethynyl)-10,20-diphenylporphinato]copper(II)

b) Mesomeric structures of the oxidation and reduction of porphyrin.

CuDEPP can be used as a high-performance and versatile electrode material for energy storage.

CuDEPP-based electrode has been used in a dual-ion-battery with graphite.

Conclusion:

A major barrier in development of Aluminium air rechargeable battery is the high self-corrosion rate of aluminium in alkaline solutions, both under open- circuit conditions and during discharge.

In order to reduce the self-corrosion of the aluminium anode, improvement in choice of electrolyte, using additives in electrolytes, and using alloying elements plays a vital role in development of rechargeable air battery.

Gel polymer electrolyte have higher conductivity as compared to Alkaline anion exchange membrane, so as to minimise leakage hazard, aqueous alkaline electrolyte needs to be solidified into a gel electrolyte.

Electrolyte additives like Dithiothreitol additive for alkaline Aluminium batteries have been used. Additives decrease the hydrogen gas evolution on anode thereby decreasing the self-corrosion of aluminium.

Metal organic framework and alloying elements further inhibit the corrosion of aluminium Anode. Different corrosion mitigation methods are studied Which helps to inhibit the corrosion .

Anode Material studied was Anatase TiO_2 for Rechargeable Aqueous Aluminium-ion Batteries.

The surface analysis in research papers is studied by SEM, back scattered electron technique and functional group is detected by FTIR technique.

Cyclic voltammetry is studied for studying measurement of current and X-ray diffraction gives the composition of battery.

Neutron powder diffraction used to study the phase and crystal structure evolution .

It is also studied that Organic energy storage materials are future candidate for energy storage .Porphyrin based active materials are used as energy storage materials .

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