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Thesis:

Simulation of species transport in metal air battery

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Dedication

I dedicate this modest work:

To my parents who have always supported, encouraged and helped me during the study period.

To my dear sisters and my dear brother.

To my promoter **Dokkar Boubakeur**. Who guided me and helped me for the success of this work

All my friends.

To all the promo Master II.

To all the staff of the University of Ouargla KASDI-MERBAH.

To all the staff of our Mechanical Engineering Department who guided me and helped me for the success of this work.

- *GOUCHENE Salim*





Thanks

First, we want to thank our GOD, our creator for having the strength to accomplish this modest work.

We would like to thank my promoter **Dokkar Boubakeur** for his understanding, his patience, his competence, these valuable orientations, these remarks based on this work,

We would like to warmly thank the rector, the Dean, the Chief Mechanical Engineering Department, the Head of Study Department, and all the staff of Kasedi Merbah University and all the workers of the University of Ouargla, who have helped during the course of my study by the care, their communications, their disposition, and that through the technical information and also the necessary means put at my disposal for the accomplishment of my project which took place in good conditions.

- *TOBCHI Mohamed Seghir*

- *GOUCHENE Salim*





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- *TOBCHI Mohamed Seghir*



List of symbols

a	=	specific interface area of the cathode, cm^2/cm^3
A	=	cross-sectional area of the cell, cm^2
		brugg Bruggeman constant
C_i	=	Is the concentration of the species in mol/cm^3
C_d	=	capacitance of the double-layer per unit area, F/cm^2
C_0	=	oxygen concentration (depends on x and t), mol/cm^3
C_0^*	=	initial oxygen concentration, mol/cm^3
C_{Li}	=	concentration of lithium in the electrolyte, mol/cm^3
D_{Li}	=	diffusion constant of the electrolyte, cm^2/s
R_c	=	reaction rate at the cathode, A/cm^2
R_Ω	=	combined resistance of the separator, Li-ions, electrons, deposit layer, and electrical contacts, Ω
G_i	=	Represents the number of moles of the species per cubic cm^3 per second formed due to other processes
μ_i	=	the electrochemical potential of a species i expressed in J/mol
N_i	=	the flux of the species in $\text{mol}/\text{cm}^2\text{s}$
K_{ij}	=	the friction coefficients
R	=	the gas constant
T	=	the temperature
C_T	=	the total concentration of the electrolyte or solution in mol/cm^3
v_i	=	the average velocity of a species i .
C_{O_2}	=	the concentration of oxygen in mol/cm^3
D_{O_2}	=	the oxygen diffusion coefficient in cm^2/s
G_{O_2}	=	represents the number of moles per cubic cm^3 per second of oxygen formed due to other processes and is equal to according to equation
R_c	=	the cathode c reaction rate
V_0	=	the open cell voltage
$\eta_c(t)$	=	the overpotential at the cathode
$\eta_a(t)$	=	the overpotential at the anode
R_e	=	the resistance of the electrolyte

I	=	the value of the discharge current
k_a	=	the reaction constant (expressed in A/cm ²)
V_T	=	the thermal voltage
β	=	the symmetry factor which is consider equal to 0.5 (therefore, $\beta=1-\beta$) in this model.
ε	=	the porosity
k_c	=	the reaction rate coefficient at the cathode (A/cm ²)
$r_p(t)$	=	the average radius of the pores
t_s	=	the transit time
k	=	geometric constant
ν	=	the kinematic viscosity
ω	=	the rotation rate
D	=	the diffusion coefficient
ρ_c	=	the mass density of carbon
q	=	A fitting parameter describing the rate at which the resistance increases with the thickness of the deposit layer,
$d_{Li_2O_2}$	=	The thickness of the deposit layer,
$d_{0Li_2O_2}$	=	Another fitting parameter that has the significance of a critical tunneling length,
R_0	=	A constant of proportionality with the dimensions of resistance.

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Abstract

In this work a type of Li-air battery is studied which has the most high current density. This kind of batteries is formed by anode of metal and a cathode of porous carbon where oxygen passes through it to ionize and react with electrodes during discharge phase. In order to study the physics phenomenon, the simplified mathematical model is chosen. Using the "Matalab" software, the effect of porosity factors, current intensity and reaction velocity on specific capacity are examined. In addition, the concentration of oxygen in the cathode layers is investigated. The obtained results are in good concordance with experimental data found in the literature.

Keywords: battery Li-air, cathode, oxygen concentration, specific capacity

الخلاصة

قمنا في هذا العمل بدراسة نوع من بطاريات الليثيوم التي تعمل على تقنية معدن-هواء ، والتي تعتبر من احسن البطاريات حيث تمتاز بكثافة كهربائية عالية. هذا النوع من البطاريات يتكون من أنود معدني وكاتود من الكربون المسامي ، حيث يمر الأكسجين من خلاله إلى التآين ويتفاعل مع شوارد المعدن أثناء عملية التفريغ. لدراسة هذه الظاهرة الفيزيائية ، اخترنا النموذج الرياضي المبسط. باستخدام برنامج "Matalab" ، حيث بينا تأثير كل من العوامل المسامية ، شدة التيار ، سرعة التفاعل على السعة النوعية للبطارية وكذلك تركيز الأكسجين في طبقات الكاتود.

كلمات مفتاحية : بطارية ليثيوم الهواء ، الكاتود ، تركيز الأكسجين ، السعة النوعية.

General introduction

Since the ancient Assyrians civilization in Baghdad, the invention of very early battery is a disputed claim, but if it was real, it was soon forgotten. Indeed, in the 18 century, Luigi Galvani observed an energy created from the contraction of his leg and iron. He called this phenomenon "animal electricity". However, Alessandro Volta, a friend and fellow scientist, disagreed, believing this phenomenon was caused by two different metals joined together by a moist intermediary. He verified this hypothesis through experiment, and published the results in 1791. In 1800, Volta invented the first true battery, which came to be known as the voltaic pile. The voltaic pile consisted of pairs of copper and zinc discs piled on top of each other, separated by a layer of cloth or cardboard soaked in brine (i.e., the electrolyte). The evolution of battery goes very fast in 20th century. Recently, the Secondary metal-air batteries can become largely commercially viable safe and efficient energy storage technology on the other hand the development of metal-air batteries takes a new important technique by these systems of increasing the density of energy [1].[2]

Metal-air batteries comprise a metal electrode (Zn, Li, Mg, Al), an electrolyte (aqueous or non-aqueous). The basic operating principle is to electrochemically reduce O₂ from the air and to oxidize the metal electrode to reversibly form solid metal oxides. In this way, the volume and weight of the battery can be significantly reduced [3]. Li-air (LAB) batteries in aprotic-electrolytes concern the precipitation of Li₂O₂. When this solid precipitates in the cathode, it can form a dense layer on the surface of the carbon and inhibit the electron transfer. As precipitation continues, whole pores in the cathode may become clogged, passivating the electrode and limiting the capacity of the cell. It has been noted that oxygen transport in aprotic-electrolytes can be a difficult factor in the performance of the LAB, particularly at higher current densities. It is well known that Li metal reacts violently with water, which previously limited the use of aqueous electrolytes for Li-air systems. Then in 2004, a vitreous ceramic layer on the Li electrode was successfully proposed to protect the metal electrode while allowing the electrochemical reaction to continue.

In this context the present work is carried out to investigate the species transport in lithium air battery. The manuscript is divided into three chapters. The first chapter contains the history, different types and industrial applications of batteries. The second chapter traits the different types of metal air batteries, their operating principles and physical characteristics. In the third chapter, an numerical simulation is carried out to examine the performance of lithium air batteries. Finally, the manuscript is finished by general conclusion and perspectives.

**General introduction to concepts
metal air battery.**

CHAPTER

I

General description.

I.1 Introduction:

A battery is a source of electrical energy, which is provided by one or more electrochemical cells of the battery after conversion of stored chemical energy. In today's life, batteries play an important part as many household and industrial appliances use batteries as their power source.

Imagine a world where everything that used electricity had to be plugged in. Flashlights, hearing aids, cell phones and other portable devices would be tethered to electrical outlets, rendering them awkward and cumbersome. Cars couldn't be started with the simple turn of a key a strenuous cranking would be required to get the pistons moving. Wires would be strung everywhere, creating a safety hazard and an unsightly mess. Thankfully, batteries provide us with a mobile source of power that makes many modern conveniences possible.

While there are many different types of batteries, the basic concept by which they function remains the same. When a device is connected to a battery, a reaction occurs that produces electrical energy.

This is known as an electrochemical reaction. Italian physicist Count Alessandro Volta first discovered this process in 1799 when he created a simple battery from metal plates and brine-soaked cardboard or paper. Since then, scientists have greatly improved upon Volta's original design to create batteries made from a variety of materials that come in a multitude of sizes. [6]

I.2 History:

The history of electro-chemical energy storage began with scientific investigations into electricity. Names such as Luigi Galvani (1737-1798) and Alessandro Volta (1745-1827) are associated with this work and live on today in terms such as "galvanic cell" and "volt". In 1789, while conducting an experiment, Galvani noticed that the legs of a frog began to twitch when they came into contact with two different types of metal. He concluded there was a connection between electricity and muscle activity.

Ten years later, Volta constructed the first simple battery. He put together alternating discs of copper and zinc in a column, with a sheet of paper soaked in a salt solution inserted between each of the layers. The "Voltaic pile" produced electricity when the plates were connected together with wire. Higher voltage could be extracted when several piles were connected in series. Johann Wilhelm Ritter (1776-1810), who worked with Goethe in the area of natural science, developed a battery in 1802, the so-called "Ritterian pile". The pile consisted of layers of copper and cardboard soaked in a table salt (sodium chloride) solution. The device could be charged with electricity and released current on discharge. The pile is considered to be the fore-runner of the accumulator, the rechargeable battery. In the following centuries work on galvanic elements continued intensively and by the dawn of the 20th century, the original battery, which could only be operated while stationary, had been developed into a supremely practical dry element. The French engineer Georges Leclanché, the German physician Dr

Carl Gassner (1855-1942) and Paul Schmidt (1868-1948) were instrumental in its development. Leclanché invented the manganese dioxide zinc cell with ammonium chloride acting as the electrolyte. The cell is still in wide use today. At a later date, Gassner and Schmidt succeeded in thickening the previously Liquid electrolytes, hence laying the foundations for transportable batteries. [7]



Fig I.1: Camille Jenatton was first to break 100km/hr speed barrier in his 1899 [7]



Fig I.2: Voltaic pile Johann Wilhelm Ritter (1776-1810) [7]

I.2.1 History of the development of the battery: [8]

1600	Gilbert (England)	First electro-chemical experimentation
1789	Galvani (Italy)	Discovery of electricity while experimenting with animals/frogs
1800	Volta (Italy)	Discovery of the Volta cell/"Voltaic pile"
1802	Cruikshank (England)	First electric battery for mass production
1802	Ritter (Germany)	First accumulator "Ritterian pile"
1820	Ampère (France)	Discoverer of electromagnetism
1833	Faraday (England)	Publication of Faraday's Law
1836	Daniell (England)	Discovery of the "Daniell elements"/galvanic cell
1859	Planté (France)	Invention of the lead acid battery
1860	Leclanché (France)	Invention of the "Leclanché cell" manganese dioxide zinc element
1899	Jungner (Sweden)	Invention of the nickel-cadmium battery
1901	Edison (USA)	Invention of the nickel metal hydride battery
1932	Schlecht Ackermann (Germany)	Invention of sintered electrodes
1947	Neumann (France)	Successful sealing of the nickel cadmium battery
1960	Union Carbide (USA)	Development of the alkaline manganese battery
1970		Development of the valve-regulated lead acid battery
1990		Commercialisation of nickel metal hydride battery (e.g. for vehicles)
1992	Kordesh (Canada)	Commercialisation of rechargeable alkaline manganese Batteries
1999		Commercialisation of lithium ion polymer batteries
2002		Limited manufacture of fuel cells (PEM, for consumer batteries and vehicles)
2006		First MP3 player with "bacteria batteries" (not yet commercially viable)
2007		First "paper batteries" (not yet commercially viable)

Table I.1: History of the development of the battery

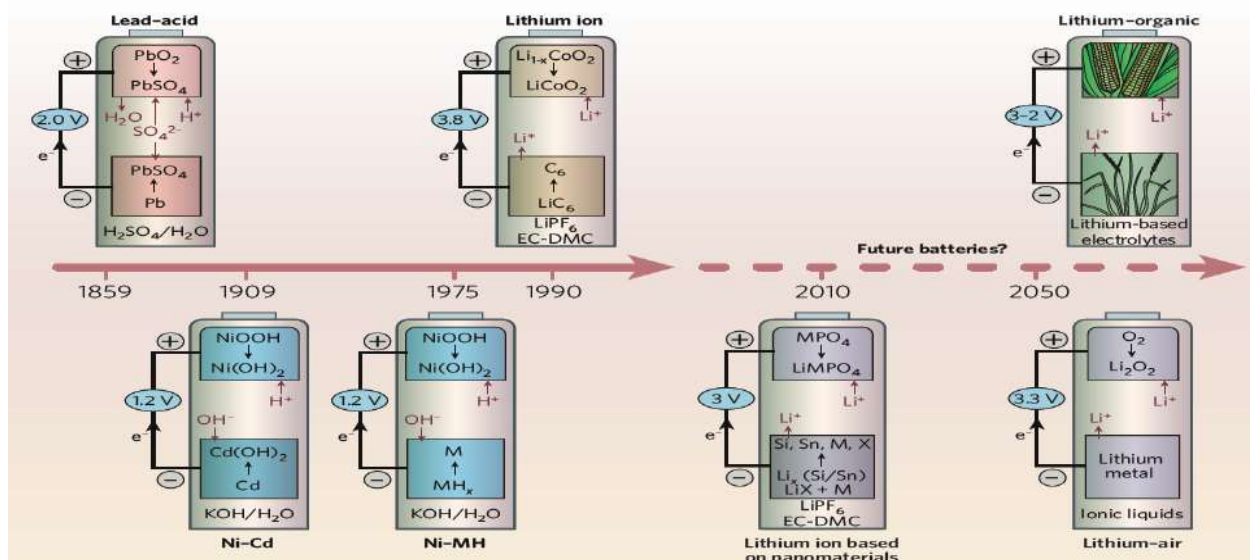


Fig I.3: The development of the battery [8]

I.3 Types of Batteries:

Batteries can be divided into two major categories, primary batteries and secondary batteries.

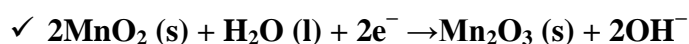
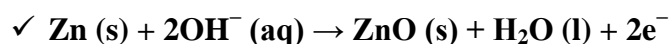
I.3.1 Primary (Non Rechargeable) Batteries:

In primary batteries, the electrochemical reaction is not reversible. During discharging the chemical compounds are permanently changed and electrical energy is released until the original compounds are completely exhausted. Thus the cells can be used only once.

I.3.2 Alkaline Batteries:

Alkaline batteries are non-rechargeable, high energy density, batteries that have a long life span. This battery obtained its name because the electrolyte used in it is alkaline (potassium hydroxide). The chemical composition features zinc powder as an anode and manganese dioxide as the cathode with potassium hydroxide as the electrolyte. [9]

The chemical reactions are:



If we compare the capacity of an alkaline cell with a zinc-chloride cell of same size, the former can provide about four to five times more energy under equal load conditions. The supply voltage level decreases over time so the minimum required voltage level for a particular load may not match the supplied voltage level and thus results in no operation. But the rate of decline of alkaline batteries is lower than the Leclanche cell, thus longer life. The typical values of voltage and current supplied

by a single alkaline cell are 1.5V and 700mA respectively. These batteries are distributed in various standard cylindrical shapes.



Fig I.4 : Alkaline batteries are non-rechargeable [9]

I.3.2.1 Applications:

Alkaline batteries are the most common type of batteries used in the world with major consumption in the US, UK and Switzerland. Designed for long lasting performance, these can be found in remote controls, clocks, and radios. The high run time makes alkaline batteries ideal for digital cameras, hand held games, MP3 players.

I.3.3 Zinc-Carbon Batteries:

Zinc-Carbon batteries are also known as dry cells (as the nature of electrolyte used in these cells is dry), which come in a composition of a carbon rod (cathode) surrounded by a mixture of carbon powder and manganese dioxide (to increase the conductivity). This whole combination is packed in a zinc container acting as the anode.

The electrolyte is a mixture of ammonium chloride and zinc chloride. The typical voltage value is a little less than 1.5V. These batteries are durable and have longer lives. Zinc-Carbon batteries can be used effectively at moderate temperature but do not work well at low temperatures. [10]

Structure of a Zinc/Carbon Cell

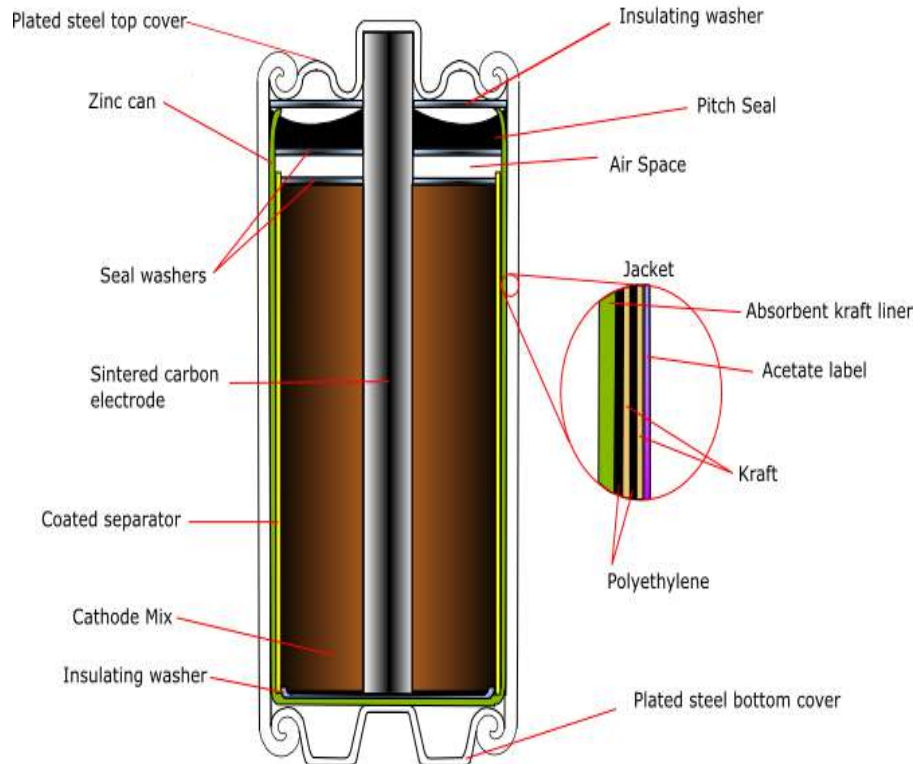


Fig I.5 : Structure of a zinc/carbon cell [10]

I.3.3.1 Applications:

These general purpose batteries are available for lower prices which is why many electronic devices are sold with these batteries included free. The basic use is in low power drain applications such as flash lights, remote controls, toys, and table clocks.

I.3.4 Mercury Batteries:

Mercury batteries are non-rechargeable batteries that contain mercuric oxide with manganese dioxide. They are deep discharge batteries and voltage level does not fall below 1.35V until 5% energy level is reached. These batteries are less popular because of low output voltage. Furthermore, mercury is toxic and can cause hazards for humans. [10]

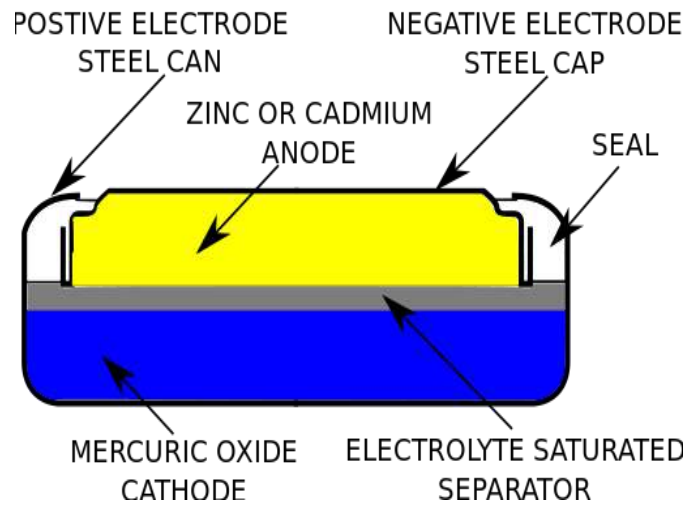


Fig I.6 : Mercury batteries non-rechargeable [10]

I.3.4.1 Applications:

The flat discharge curve makes this battery useful for photographic light meters and electronic devices such as to run the real-time clock of CPU.

I.3.5 Secondary batteries in secondary batteries, the electrochemical reaction is reversible and the original chemical compounds can be reconstituted by the application of an electrical potential between the electrodes injecting energy into the cell. Such cells can be discharged and recharged many times.

I.3.6 Lead-Acid Batteries:

Lead-acid batteries are the rechargeable kind of batteries invented in the 1980s. These large, heavyweight batteries find the major application in automobiles as these fulfill the high current requirements of the heavy motors. The composition of Lead-Acid battery changes in charged and discharged states. A combination of Pb (negative) and PbO_2 (positive) as electrodes with H_2SO_4 as electrolyte in charged form and PbSO_4 and water in discharged form. [10]

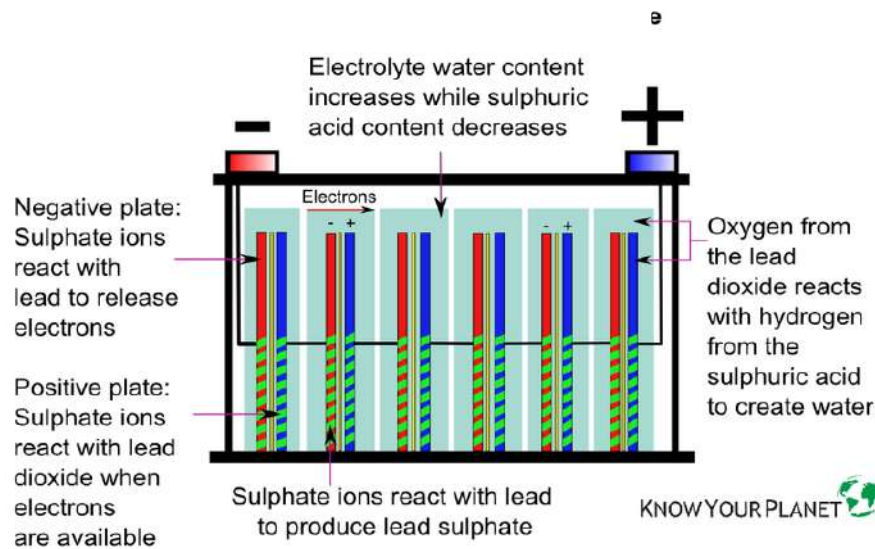


Fig I.7: Lead-acid batteries are the rechargeable [10]

I.3.6.1 Applications:

The major application of lead acid battery is in starting, lightning, and ignition systems (SLI) of automobiles. Its other form, wet cell battery is used as backup power supply for high end servers, personal computers, telephone exchanges, and in off grid homes with inverters. Portable emergency lights also use lead acid batteries.

I.3.7 Lithium and Silver Oxide Batteries:

Lithium batteries are rechargeable (secondary) batteries, where lithium in its pure ion compound form is used. Depending on the design and chemical compounds used, lithium batteries can produce voltages from 1.5 Volts to 3.7 Volts. The most common type of lithium battery used in consumer applications uses manganese dioxide as cathode and metallic lithium as anode. Compared to ordinary zinc-carbon batteries or alkaline batteries, the voltage production of lithium cell is twice from them.

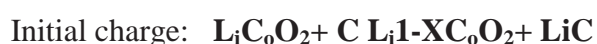
Silver oxide batteries are expensive, small to large sized primary cells that offer better run time than alkaline batteries. They are usually suitable for powering low-current electrical devices. They use silver oxide as positive (cathode) electrode, zinc as negative (anode) electrode plus alkaline electrolyte, normally Potassium hydroxide (KOH) or Sodium Hydroxide (NaOH). [10]

I.3.7.1 Applications:

These long life batteries are used in portable consumer instruments like calculators, iPods, digital diaries, wrist watches and stop watches, toys, and artificial pacemakers. Lithium cells can also be used as a replacement of alkaline batteries in many devices, such as cameras and clocks. Although they are more expensive, lithium batteries will provide much longer life. Silver Oxide batteries are used in military and submarines.

I.3.8 Lithium Ion

Lithium ion batteries have many applications and are the system of choice if a high energy density is required. Rechargeable lithium batteries do not contain lithium in its metal form. Their main use is in telecommunications and portable computers. As industrial batteries, the lithium ion system is used in hybrid electrical vehicles and vehicles with the new wire harnesses. Lithium ion accumulators are not compatible with NiCd or NiMH accumulators; they require a specific method of charging and cell management although lithium batteries also function like galvanic cells, the active materials do not react chemically. Instead, Lithium ions are incorporated into the positive electrode and the negative electrode. During charging, ions are in effect pumped from one electrode to the other. They are, so to say, swapped between the positive and negative interface material. This system is a safe alternative to lithium metal galvanization. The energy density is mainly determined by the cathode material – cobalt oxide is commonly used today, which is suitable for a maximum of 180 watt hours per kilogramme. Lithium nickel cobalt (LiNiCo) can produce an energy density of maximum 240 Wh/kg. The principal reaction equation can be represented as:



Of all the rechargeable systems, lithium ion batteries have the greatest energy density per volume or weight. As with other secondary systems, the period between recharging depends on the application. The energy density of lithium ion batteries is typically double that of standard nickel cadmium batteries. In addition there is potential for even higher energy densities in the future. The resilience aspect is good and they are similar to nickel cadmium batteries regarding discharge. A high voltage of 3.6 V per cell means unicellular batteries can be constructed. Most mobile phones function with an unicell. A nickel based battery requires three 1.2 V cells in series to achieve the same voltage. Rechargeable lithium batteries have no memory or lazy effect. To store the batteries, the majority of manufacturers recommend 40 percent charge status and a cool environment. [10]

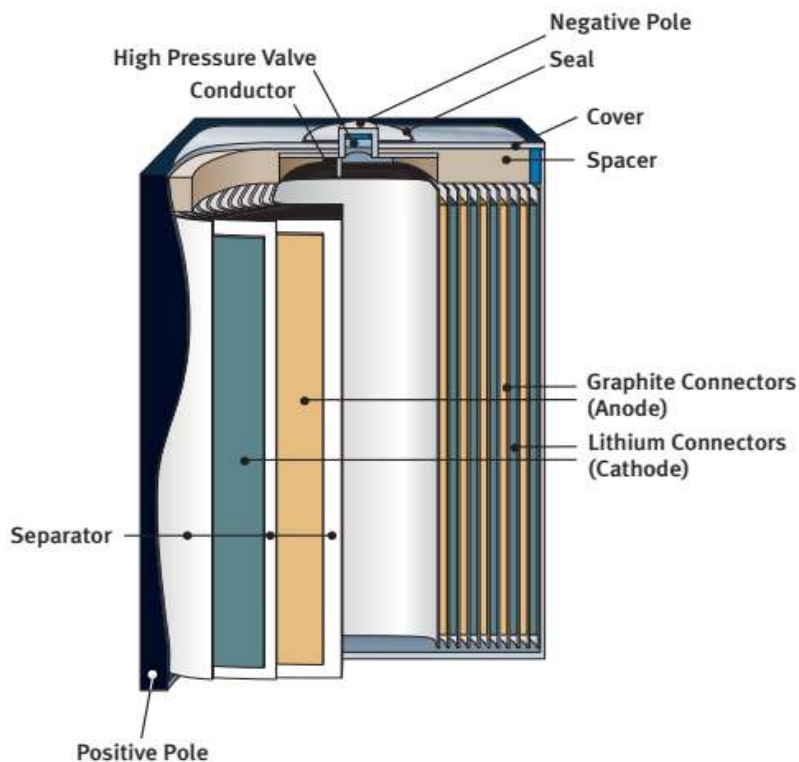


Fig I.8 : Design Lithium Ion [10]

I.3.9 Lithium Polymer (Li-P)

For several years now, academic and industrial scientists have been working on polymer electrolytes to replace conventional liquid organic electrolytes and simultaneously make the classic separator redundant. The lithium polymer battery differs from other rechargeable lithium batteries by the electrolyte it uses. The electrolyte is a plastic-like layer, which cannot conduct electricity, but allows the exchange of ions (exchange of electrically charged atoms or groups of atoms).

The polymer electrolyte replaces the traditional porous separator element soaked in electrolyte. Without a liquid electrolyte these accumulators are absolutely leak-free and aluminum or metallic plastic foils can be used instead of a metal as housing for the cell.

The dry polymer solution simplifies manufacture, improves robustness, safety and also permits a slender form. It can be produced in any shape to occupy the empty space in appliances. Even extremely flat, foil-like shapes are possible. With a cell thickness of about one millimeter, device designers can let their imagination run wild when it comes to the shape, configuration and size of the battery.

However, the dry lithium polymer suffers from poor conductivity. Internal resistance is too high to deliver the power peaks necessary for modern communication devices, which leads to problems with the hard disc of portable computers. Heating the cells to 60°C or more improves conductivity, but is a specification which cannot be implemented in portable applications. [10]

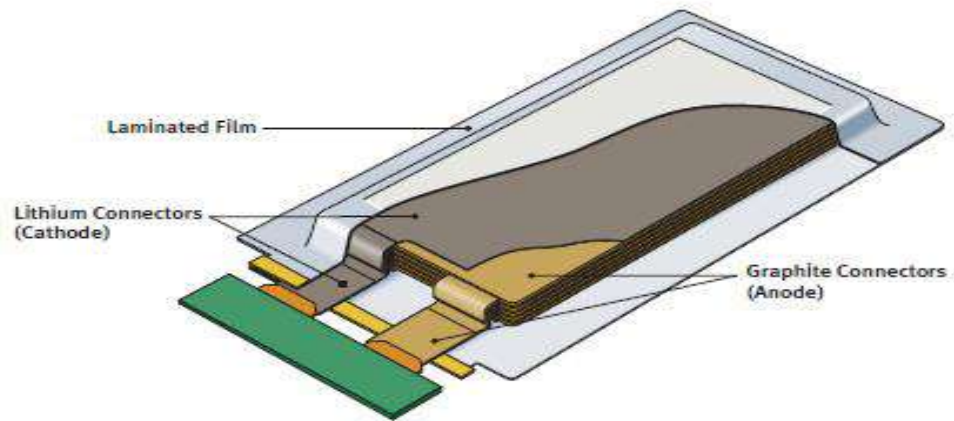


Fig I.9: Design Lithium Polymer/Li Polymer [10]

CHAPTER

II

Metal-air Batteries.

II.1. introduction

The metal-air batteries it has a advancement of renewable energy production, In this study The use of theoretical models can improve the understanding of researchers on electrochemical systems, use more efficiently we are looking at Modeling methods of secondary rechargeable batteries in our study

II.1.1 Physical principles

A Metal-Air (M-Air) battery system is an energy storage system based on electrochemical charge/discharge reactions that occur between a positive “Air Electrode” (cathode) and a negative “Metal Electrode” (anode). The negative electrode is typically made of metals such as Li, Zn, Al, Fe, or Na, while the positive usually contains some form of porous carbon material and a catalyst. The electrolyte can be of aqueous or non-aqueous nature as is typical for Li-Air systems. Oxygen from the atmosphere diffuses through the porous carbon electrode, where a catalyst facilitates its reduction while the metal is oxidized in the anodic reaction. In the M-Air concept, most of the cell volume is occupied by the anodic material itself, thus leading to high energy densities. [11]

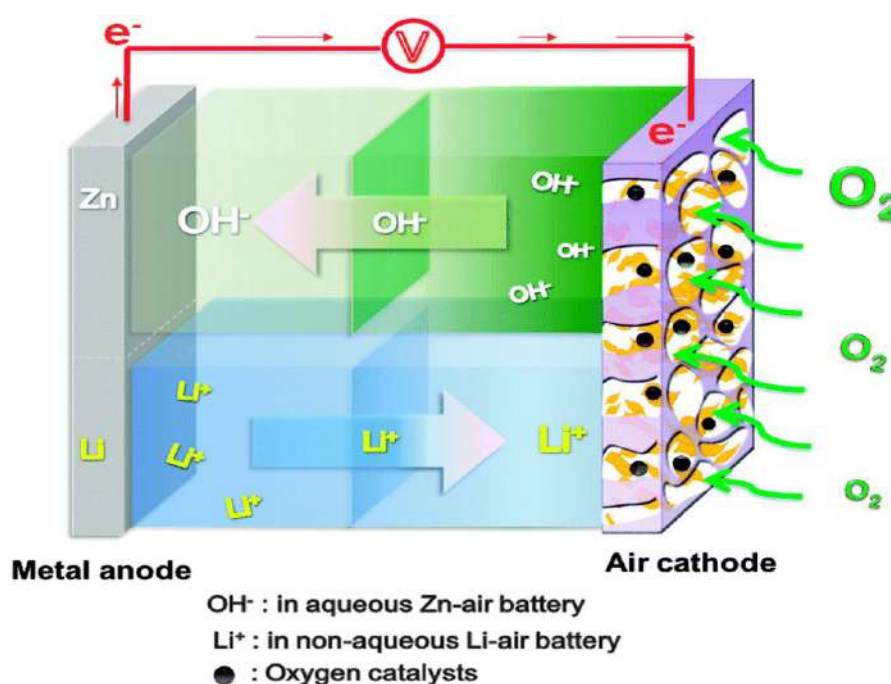


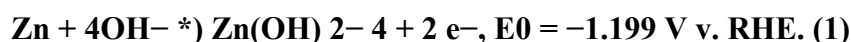
Fig II.1: Metal-Air (M-Air) battery system

II.1.2 Zinc-air battery:

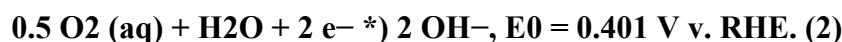
In this section, we present a summary of the working principle of ZABs and discuss the main challenges hindering the development of electrically-rechargeable Zn-air systems.

II.1.2.1 Working Principle:

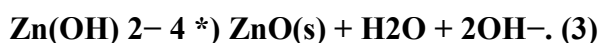
In their most common configuration, Zn-air batteries contain a metallic Zn electrode, porous separator, circa 30wt% aqueous KOH electrolytes, and a bi-functional air electrode (BAE). The BAE consists of a porous substrate and a bi-functional air catalyst (MnO_2) to facilitate the oxygen-reduction and oxygen-evolution reactions (ORR, OER) [12]. The design of the BAE is similar to gas, diffusion layers (GDL) from fuel cell applications. The porous BAE substrate contains carbon fibers and binder with mixed hydrophilic and hydrophobic properties to promote the formation of the so-called three phase boundary, while hindering the electrolyte from flooding out. The Zn electrode is often a paste consisting of zinc metal powder, electrolyte, and binder. The capacity of the cell is determined by the Zn electrode, which is designed in such a way as to include as much active material as possible while minimizing the effects of shape-change and electrolyte concentration gradients. Aqueous KOH is the most common electrolyte for Zn-air batteries due to its high conductivity (circa $600 \text{ mS}\cdot\text{cm}^{-1}$). An operational schematic of a ZAB in alkaline electrolyte is shown in Figure II.2. When the cell is discharged, the Zn electrode is electrochemically oxidized to form $\text{Zn}(\text{OH})_2$ – 4 (Zincates) complexes,



Oxygen gas enters the cell through the BAE and dissolves into the electrolyte, where it is reduced to form OH^- ions,



When the saturation limit of zinc in the electrolyte is exceeded, solid ZnO precipitates mainly in the anode and the battery achieves a stable working point



When the cell is charged, ZnO dissolves, zinc is redeposited at the Zn electrode and oxygen gas is evolved in the BAE. The overall cell reaction is given by

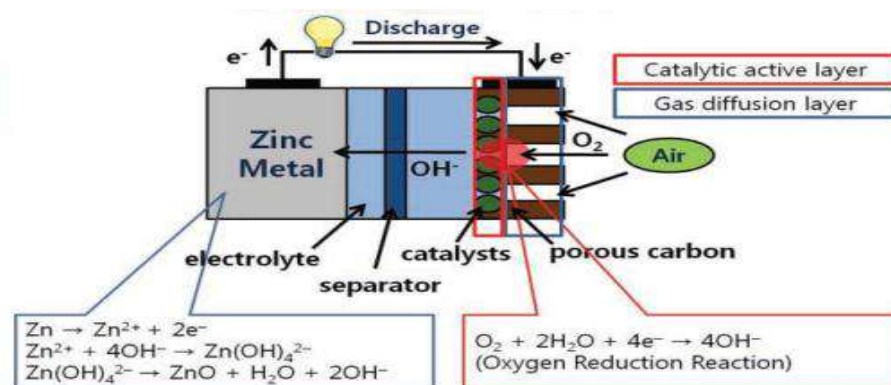
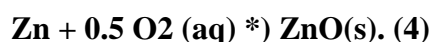


Fig II.2: Operational schematic of an alkaline zinc-air battery. [12]

The open-circuit voltage of a ZAB in 30 wt % KOH is 1.65 V. The high conductivity of the electrolyte, high mobility of OH^- , and reasonable kinetics of the ORR give the cell a nominal discharge voltage of 1.2 V at current densities of circa $10 \text{ mA} \cdot \text{cm}^{-2}$. The molar volume of ZnO is 60% larger than metallic Zn, which causes the cell to expand during discharge. Even so, ZAB button cells demonstrate a practical energy density on the order of 1000 WhL^{-1} [13].

II.1.3 Aluminium-air batteries

Al-air batteries produce electricity from the reaction of oxygen in the air with aluminium. They have one of the highest energy densities of all batteries, but they are not widely used because of problems with high anode cost and byproduct removal when using traditional electrolytes. This has restricted their use to mainly military applications. However, an electric vehicle with aluminium batteries has the potential for up to eight times the range of a lithium-ion battery with a significantly lower total weight. [14]

Aluminium-air batteries are primary cells, non-rechargeable. Once the aluminum anode is consumed by its reaction with atmospheric oxygen at a cathode immersed in a water-based electrolyte to form hydrated aluminum oxide, the battery will no longer produce electricity. However, it is possible to mechanically recharge the battery with new aluminum anodes made from recycling the hydrated aluminum oxide. Such recycling would be essential if aluminum-air batteries are to be widely adopted. Aluminum-powered vehicles have been under discussion for some decades. Hybridisation mitigates the costs, and in 1989 road tests of a hybridized aluminum-air/lead-acid battery in an electric vehicle were reported. An aluminum-powered plug-in hybrid minivan was demonstrated in Ontario in 1990. In March 2013, Phinergy [15] released a video demonstration of an electric car using aluminium-air cells driven 330 km using a special cathode and potassium hydroxide. On May 27, 2013, the mass media evening news broadcast showed a car with Phinergy battery in the back, claiming 2,000 kilometres (1,200 mi) range before replacement of the aluminum anodes is necessary.

II.1.4 Lithium batteries

Nowadays, lithium batteries have paid attention and increased global demand for the energy storage domain. The unique properties of lithium element are presented in Table II.1. Lithium has the highest capacity, the lowest electrochemical potential (-3.04 V/SHE) and provides, for a given positive, the highest energy density. Two types of lithium batteries have been developed: batteries based on Lithium metal negative, Li, and batteries based on graphite, LiC_6 lithium ion. Shifting from Li to LiC_6 was motivated by the instability of Li_0 , especially during charging. There is roughly an order of magnitude between the theoretical capacity of Li_0 and LiC_6 but it must be

emphasized than Li₀ is used in large excess with regard to the stoichiometry i.e. often 5 to 7 excess, so the gap in practical capacity strongly decreases. Li₀ has other advantages, namely (i) its electronic conductivity and (ii) its mechanical strength and ductility; these advantages making useless the use of carbon black and polymeric binders and allowing its easy calendaring. Although slightly lower in energy density than lithium metal, lithium-ion is safe, provided certain precautions are met when charging and discharging. In 1991, the Sony Corporation commercialized the first lithium-ion battery. Other manufacturers followed. The energy density of current lithium-ion batteries is typically triple of that of the standard NiCd, some prototypes reaching specific energies around 200 Wh/kg and some Lithium properties listed in the following table [15]

Properties	Lithium
Equivalent weight (g/equiv.)	6.94
Reversible potential (V)	-3.045
Electronegativity	0.98
Specific gravity (g/cm ³)	0.53
Theoretical specific capacity (A.h/kg)	3,860

Table II.1: Properties of Lithium

II.1.5 Lithium-Air Battery:

Today, lithium-ion batteries are widely used in our daily life as power sources for laptop computers, mobile phones, music players, digital cameras, and many other electronic devices. Despite their success and widespread usage, there is an increasing need for batteries with higher densities than today's commercialized batteries, especially in the automotive industry. Herein, lithium-air batteries come to the forefront. A lithium-air battery could potentially provide three to five times higher energy densities than conventional Li-ion batteries (Because the driving range of an electric vehicle will be extended by using lithium-air battery and become comparable to gasoline vehicles, they captured worldwide attention in the past few years. If the system is successfully developed, the dependence on gasoline will be decreased and thus it will be a part of a solution for global climate change due to emissions, of the world's primary energy demand is covered by oil, which results in approximately emission with a big influence on global climate change. [16]

The specific capacity of lithium-air batteries are the highest among all kind of batteries (see Table. Together with other advantages, this makes lithium-air batteries one of the most attractive alternative energy storage systems. Although the first studies were done in 1996 by Abraham et al., most of the work was performed in the past few years. Studies mainly focused on cathode and electrolytes; different types and structures of materials, catalysts, and electrolytes were investigated in order to improve the performance and to overcome some obstacles.

Currently, there are different versions of lithium-air batteries based on the electrolyte:

- ✓ Non-aqueous Li-air battery utilizing organic liquid, polymer or ionic liquid electrolytes,
- ✓ Aqueous Li-air battery,
- ✓ Solid-state Li-air battery utilizing a conductive inorganic solid electrolyte separator,
- ✓ Mixed Li-air battery utilizing both non-aqueous and aqueous electrolytes. Since lithium-air batteries are not the scope of this thesis, only the non-aqueous electrolyte type is discussed in detail because it attracts the widest interest.

A) Aqueous Li-O₂ batteries

The schematic of a aqueous lithium-air battery is shown in **Figure II.4**. Although aqueous Li-O₂ batteries have slightly smaller theoretical capacities, they are an interesting alternative to the aprotic system. Aqueous LiOH solution is the most common electrolyte for this battery type. It offers the advantage of a high ionic conductivity and a large stability window to operate the cell [17]

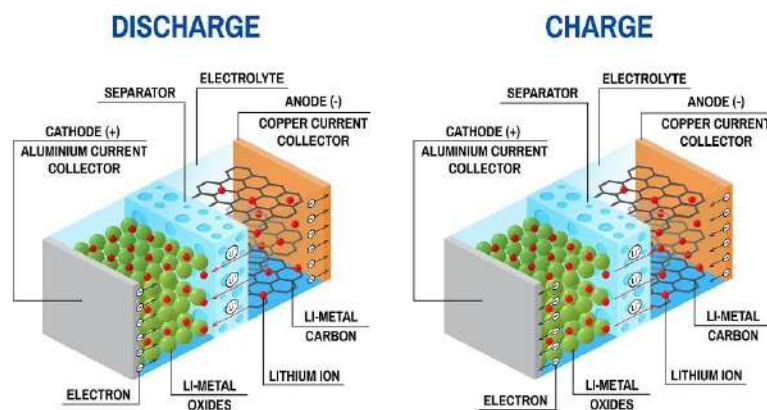


Fig II.3: Aqueous lithium-air battery [17]

b) Non-aqueous lithium-air battery

The schematic of a non-aqueous lithium-air battery is shown in **Figure II.4**. Intense research on this type of battery started in 1996 when Abraham *et al.* [17] demonstrated the use of organic electrolytes for Li-O₂ batteries. Since then the aprotic system attracted the most attention in the community and the majority of published work was done on this type of battery

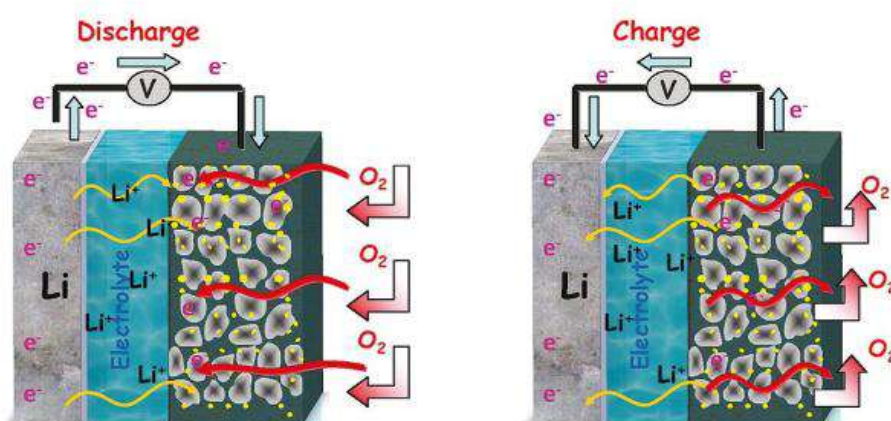


Fig II.4: Non-aqueous lithium-air battery [17]

II.1.5.1 Capacity of a lithium-air battery:

The operating potential and the charging potential, as well as the over potentials are shown in the figure. The difference between the open circuit voltage (OCV) and the operating voltage is defined as discharge over potential. The difference between the charging potential and the OCV is called charge over potential. One can see in **Figure (II.5)** that the discharge potential is around due to the activation and ohmic losses. Also, the cell potential increases up to when the cell is charged with a constant current. The over potentials mentioned above are challenges for the researchers. In order to improve the performance of the battery, people try to overcome these over potentials by using electro catalysts. By using catalysts, not only the over potentials will be reduced, but the electrical and thermodynamic efficiency together with the discharge capacity will be increased remarkably. [18]

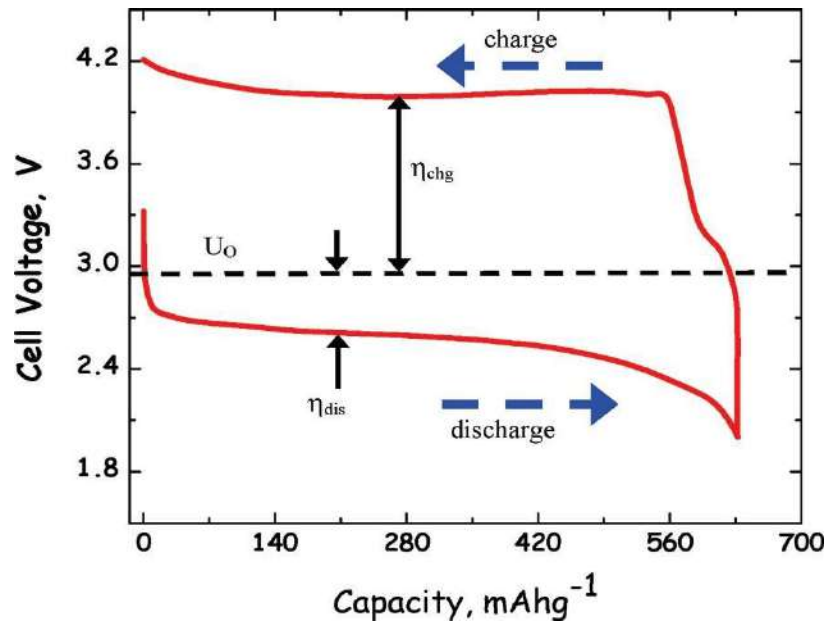


Fig II.5: Capacity according to cell voltage [18]

II.1.5.2 The different components:

A lithium-air cell consists of a separate lithium anode and air cathode by a membrane soaked with electrolyte.

- ✓ The anode is made of metallic lithium. Due to its very low potential, lithium metal makes it possible to reach high cell voltages. In addition, the energy densities obtained with a lithium anode are important because the mass capacity of lithium is very high.
- ✓ The separator is an electronic insulator. Ideally, it must be very thin, highly tortuous to hinder dendritic growth, and chemically inert.
- ✓ The electrolyte may be aprotic or aqueous depending on the architecture studied. It contains a dissolved lithium salt.
- ✓ The air cathode is composed of carbon with a high specific surface area, a catalyst and a binder, deposited on a substrate

II.1.6 Applications M-Air batteries:

Due to their high scalability and energy density, M-Air batteries can be used in a large variety of applications:

- ✓ Large-scale stationary energy storage applications
- ✓ Preferably in combination with renewable wind or solar
- ✓ Power systems to compensate the intermittent nature of these renewable power sources
- ✓ Transportation: due to its high energy density, M-Air batteries would increase the autonomy of the current electric vehicles
- ✓ Renewable generation: smoothing and shaping functions associated with voltage and frequency support to ensure better integration of large renewable plants into the electricity system

II.1.7 The major advantages and disadvantages are summarized below:

II.1.7.1 The advantages:

- ✓ High energy density,
- ✓ Flat discharge voltage,
- ✓ Long shelf life (dry storage),
- ✓ Non toxic (on metal use basis),
- ✓ Low cost (on metal use basis).

II.1.7.2 The disadvantages:

- ✓ Dependent on environmental conditions:
 - Drying out limits shelf life once opened to air,
 - Electrolyte flooding limits power output,
- ✓ Limited power density,
- ✓ Limited operating Temperature.

II.1.8 Specific energy:

Batteries built to harness metallic oxidation reactions, using atmospheric oxygen as a cathode, have been a prized goal of energy storage research for decades. Including the mass of the oxygen reactant, metal-air batteries have exceptionally high materials level theoretical specific energies, which in the case of Li-air exceed that of current lithium-ion battery couples (NMC/graphite, by nearly a factor of ten). However, there are numerous challenges that must be overcome to enable reversible cycling of metal-air cells with high energy efficiency, as well as challenges in system design to take advantage of the intrinsically high energy. Currently, the system-level specific energy and energy density are difficult to assess, due to lack of detail as to the mass/volume of complete cells and balance of plant that would together constitute a practical system. Several metal/air couples have been evaluated for use in rechargeable batteries, as indicated. While Zn-air batteries have been used since the 1970's as cheap, high-energy primary (non-rechargeable) cells, no secondary (rechargeable) metal-air system has yet been commercialized. The bulk of research has been aimed at the lithium-air system due to its exceptionally high theoretical specific energy. A comparison with the practical energy density of gasoline in modern cars is useful. The tank to wheels efficiency of gas-powered cars is today about 17%, resulting in a practical gasoline energy density of 2244 Wh/kg (theoretical energy density of 13,200 Wh/kg). The battery to-wheels efficiency for current lithium-ion powered EVs is about 50%, and would likely be lower for rechargeable metal-air due to lower roundtrip efficiency. Assuming 40% battery-to-wheels efficiency in an optimized metal-air system, the system-level energy density required for parity with gasoline is 5610 Wh/kg. This exceeds the theoretical specific energy of all but Li-air, and in all cases, [18]

Metal	Theoretical Specific Energy (Wh/Kg) Including Oxygen Weight	Demonstrated
Lithium	5,200	Limited Reversibility
Aluminum	4,300	Primary Cell
Zinc	1,090	Limited Reversibility
Silicon	3,960	Primary Cell
Gasoline (Reference)	13,200 (2244 Practical)	

Metal/Air cell Data

Silicon data based on specific energy given in, recalculated to include oxygen weight

Table II.2: Represent Theoretical Specific Energy (Wh/Kg) Including Oxygen Weight

II.1.9 Choice of metal air battery

The Li-air battery, once fully developed, could have specific practical energies of 1000-3000 Wh kg⁻¹, also, the Li-air cell is electrically rechargeable (much more than the Zn-air battery). For this we have to choose the Li-air battery based on:

- ✓ The specific energy higher than the Zn-air battery (3842 mAh g⁻¹ for lithium, vs. 815 mAh g⁻¹ for Zinc),
- ✓ The voltage of the Li-O₂ is two time higher than the alkaline electrolytes is 2.91V (compared to 1.65 for Zn-O₂),

System level values will be significantly discounted from the values in Fig II.6. The possibility of exceeding the long term targets as well as the energy density of advanced lithium ion by a factor of several at system level has driven much recent research in metal-air. [18]

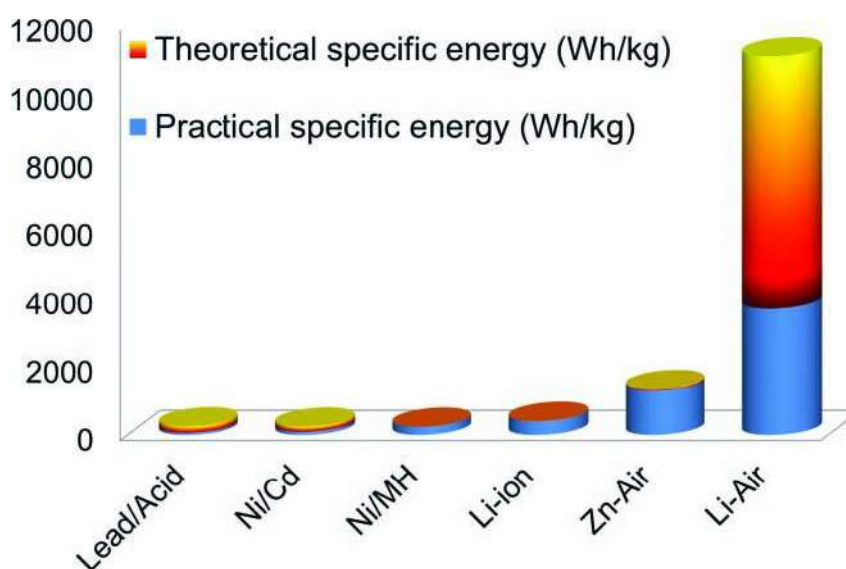


Fig II.6: Theoretical and practical energy densities of various types of rechargeable battery [18]

CHAPTER

III

**Modeling of Li-air
Batteries.**

General conclusions

In this study, the Li-air battery has investigated which has exceptionally high specific energy due to the high specific energy of lithium and the inexhaustible oxygen supply of the ambient air. Although, the high specific capacity of lithium-air battery, but, there formation of binary lithium oxide (Li_2O_2) which presents irreversible deposit inside cathode porous media.

A one-dimensional model was developed to study the various properties of Li air batteries. Mainly, the discharge current, the effects of electrode thickness and the distribution of the porosity in the electrode are examined. Advanced studies on transport phenomena have not yet fully exploited the great potential of Li-Air batteries. This is mainly the result of limiting the mass transfer of the cathode electrode.

The resistivity of the deposit layer provided by reaction products has great effects on the discharge characteristics of Li-air batteries. In this matter the investigation shows an important voltage drop according to specific capacity.

The analysis of discharge curves shows that cathode porosity has an important effect on specific capacity of battery. But, the reaction rate has more influence on battery voltage.

The diffusion of oxygen plays an important role in to drive the reactant inside the cathode. This characteristic encourages the chemical reaction which contributes to improve the battery performance.

Finally, for future works, we recommend for deep studies and detailed analysis, to overcome the problem of Li_2O_2 deposit in order to improve the battery performances.

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