

# **A New Insight into Lithium Air Batteries**

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THESIS

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*To my lovely family . . .*

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## LIST OF ABBREVIATIONS

EV	Electrical Vehicle
PEV	Plug-In Electric Vehicles
HEV	Hybrid Electric Vehicles
ICE	Internal Combustion Engine
ORR	Oxygen Reduction Reaction
OER	Oxygen Evolution Reaction
SEI	Solid Electrolyte Layer
IL	Ionic Liquid
GDL	Gas Diffusion Layer
GDE	Gas Diffusion Electrode
ICF	Initial Complex Formation
EMIM	1-Ethyl-3-methylimidazolium
DMSO	Dimethyl sulfoxide
IPA	Isopropyl alcohol



## SUMMARY

Environmental pollution and greenhouse gas emissions have been a problem since technologies were born but it has become an even greater conflict in the last decades. For that reason, the decrease in conventional energy resources pushed the industrial and technological world to look for a new concept of energy supply that is both cleaner and renewable. Reducing  $CO_2$  quantity in the air could be one of the first goals of this scientific research and battery technology could have suitable effects for this problem, as they can store energy in chemical form and replace fossil fuel energy supply.

Previously, the possibility to store energy by mean of Lithium-based battery was discovered. Recently, it has been shown that more performing Lithium-air batteries could be the new technology that may possibly replace the current Li-ion energy-storing concept. It has been extensively proven that commercial Lithium-air battery could be designed, substituting precious metal catalysts such as Pt with more affordable materials such as  $MoS_2$  or  $WSe_2$ .

This research will be focused on both Lithium-air, reporting many crucial aspects of the battery performances such as reversibility and efficiency. Moreover, the report will analyze in detail the effects of  $CO_2$  on battery performances when introduced to the mixture as an impurity in order to simulate real working conditions.

## CHAPTER 1

### INTRODUCTION

#### 1.1 A general overview of the energy storage panorama

This work will analyze the current status and the future challenges of energy storage by means of Lithium-air battery technology. In this chapter we will briefly discuss the main sources of pollution emissions, focusing the attention especially on  $CO_2$  as a pollutant. Moreover, we will analyze the evolution of electric vehicles (EV) and their future possible applications in the transportation field as well as providing a general overview about the current panorama of the battery technology.

Recent research showed that the level of  $CO_2$  has dramatically increased in the last couple of decades. The fact is due to many causes, such as democratic growth, higher energy demand and technology development. As a matter of fact, to satisfy the incredibly high energy demand, our society made full use of fossil fuels, inevitably leading to the release of pollutants such as carbon dioxide, sulfur dioxide and nitrogen oxides.

Carbon dioxide is naturally present in atmospheric air with more than 300 billion tons but, since the first industrial revolution, its percentage has increased and it has fluctuated from somewhere between 280 ppm and 350 ppm. The ultimate problem is that the percentage has increased even more in the last ten years, reaching a level of 400 ppm in 2015 [1].

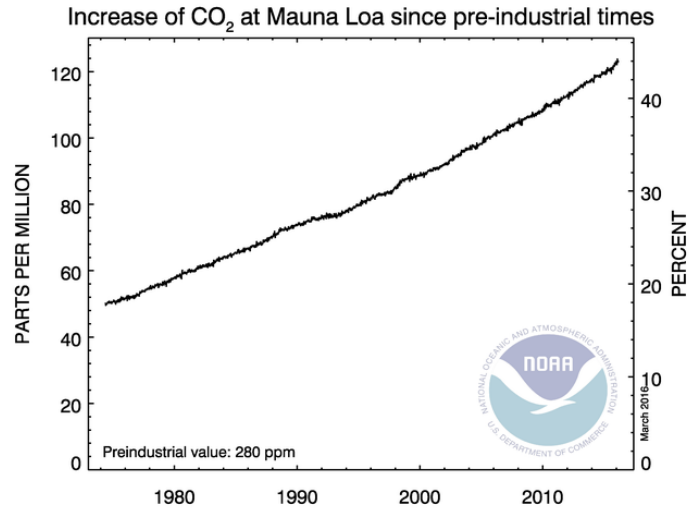


Figure 1: Carbon dioxide growth from 1958 until 2014 at Scripps Mauna Loa Observatory. Reprinted with permissions.

Studies confirm that the most common source of carbon dioxide emissions is fossil fuels: in 2011 alone, its use created 33.2 billion tons of carbon dioxide emissions in the entire world [2].

Electricity, heat and transportation are the three economic sectors that release pollutants by means of using coal, natural gas or oil. Particularly, transportation produces more than 22 % of CO<sub>2</sub> (Figure 2), and its contribution to pollution is constantly increasing, especially in the automotive field, which represents somewhere around 72 % of carbon dioxide production in its sector.

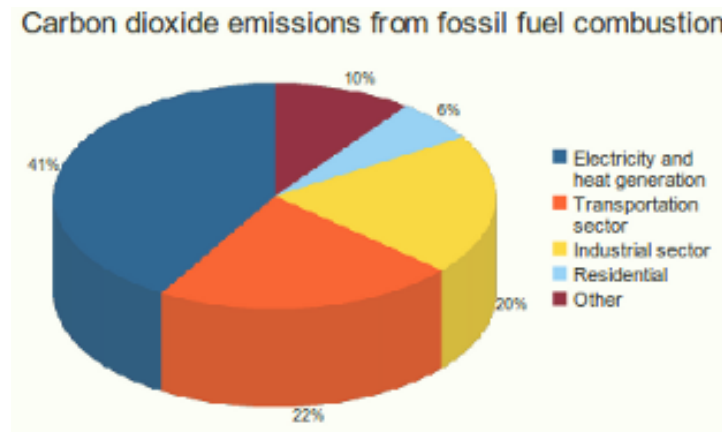


Figure 2: Carbon dioxide Emissions from Fuel Combustion (2012), International Energy Agency. Reprinted with permissions

For that reason, in order to reduce  $CO_2$  emissions, many companies and different governments made investments of over billions of dollars in order to limit the internal combustion engine (ICE) transportation by substituting it with electric vehicles (EV).

EVs could be a possible alternative to the ICEs. Even if the efficiencies of these engines are increasing and the exhaust gases emitted are decreasing more and more, EVs can ensure a higher air quality, greater energy savings and lower environment pollution. This is the reason why more and more companies started to get involved in this new concept of car and finally started to produce EVs— as more than 410,000 legal plug-in electric cars have been sold in the United States between 2008 and December 2014 [3].

Mainly, Electric Vehicles are divided in two groups. The first one is the Hybrid Electric Vehicles group (HEVs) and the second one is the Plug-In Electric Vehicles (PEVs). Hybrid Electric Vehicles are a combination of both battery energy supply and internal combustion engines that are used to supply energy after the battery runs out. On the other hand, Plug-In Electric Vehicles run only on their battery energy supply. Nowadays, the most popular electric plug-in cars are Nissan Leaf (89,591 units), Chevrolet Volt (88,750 units) and Tesla Model S (63,161 units) [4].

Even though the growth of new electric car technology has been considerably high in the last five years, the total number of electric cars that have been put on the road are still very low in comparison to the internal combustion engine. In the State of Union Address of 2011, President Barack Obama announced his plan to reach the quantity of one billion EVs sold in the United States before 2015. Unfortunately, the goal has not yet been reached and experts say that we will not reach that amount before 2020. Indeed, even if the government financed some companies with several millions of dollars by federal or state incentives in order to increase their productivity, the total number of the EVs sold will still remain quite low, not even reaching the forecast.

The main factor that continues to slow down the growth of EVs are their high prices. The electrical vehicle cannot be considered as a mass-market vehicle because its price average is \$31,000 or more, as demonstrated in a recent study by Salim Morsy of Bloomberg New Energy Finance. The problem is that more than half of the price of a single electric vehicle comes from the battery. An average battery of 600-700 pounds costs from 12 to 15 thousand dollars,

which would be somewhere around 600 to a 1000 \$/kWh. Even if the price of maintenance for the ICE is higher, economically speaking, if we compare an EV to a ICE vehicle, it is still not worth the cost.

This is the reason why research on the battery is going so fast and lot of researchers and companies are putting in their individual efforts. To provide an example, in no more than five years, Tesla is forecasting to dramatically decrease the price of the battery while also increasing their performances. This is the only way to decrease the price of the electric cars and make them affordable for everyone, since the other costs are the same of CE cars.

The second factor that really slows down the business of EVs is the potential range. A Tesla Model S has a battery pack two meters long and 1 meter wide: even if it is huge and very heavy (more than 500 kg), the total range before you have to recharge your vehicle is less than 300 miles. Moreover, the charge takes a incredible longer time compared to a common internal combustion engine vehicle.

We took Tesla Model S battery as an example because it is currently one of the most efficient batteries we can find in a commercial car. A long time has been necessary to achieve this point, but the battery technology has been widely improved in the last decades; the first affordable battery we can consider suitable for hi-tech devices was lead-acid based, which was huge and had low performances. Some years later, the *NiCad* (Nickel- Cadmium) and *NiMH* (nickel metal hydride) was discovered, and finally we discovered the modern and high performing Lithium-ions battery. Currently, they are the replacement of the lead-based batteries and they are the

most popular and commonly used; most of the technologies, such as phones, laptops, vehicles and every electronic device that needs a battery to run, works with that.

The Lithium-ions battery is suitable for these kinds of appliances since it has a quite high energy density, a tiny memory effect and a good efficiency-reversibility. The first Lithium-ion battery was discovered by M.S. Whittingham while he was working with Exxon, in 1970 [5]. From 1970 until 1991, many breakthroughs made the battery performances noticeably increase until the battery was finally commercialized by Sony. After that, many improvements were made until Amprius Corp reached an energy density that was more than  $650 \text{ Wh/L}$  in 2014, which remains one of the highest energy densities we have ever gotten from a Lithium-ions battery.

Before going into details about the energy a battery can deliver, it is important to define some general properties of the energy storage. The energy density is the amount of energy that can be stored in a system related to its volume or its weight. Its unit of measure in *SI* unit is  $J/m^3$  and it is a specific quantity.

Also, the capacity is the amount of current that a battery can supply for a defined time. Its unit of measure is  $Ah/kg$  and, for example, a  $1 \text{ kg}$  battery with a capacity of  $100 \text{ Ah}$  can provide a current of  $5 \text{ A}$  over a period of 20 hours or it can provide a current of  $10 \text{ A}$  over a period of 10 hours; that means the time to reach the complete discharge of the battery is directly related to the discharge rate. The common way to talk about the charge stored in a battery is to refer to the whole battery volume or weight.

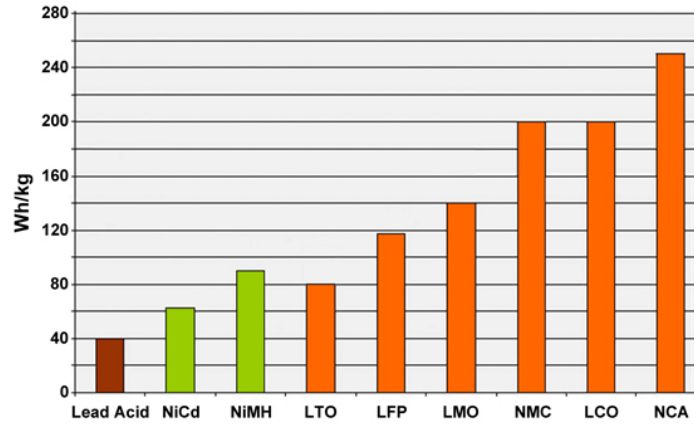


Figure 3: Specific energy densities of different Lithium-ions batteries relative to the electrodes materials. Reprinted with permissions ([www.batteryuniversity.com](http://www.batteryuniversity.com))

As previously stated, the best performance for a commercial product in the automotive field has been obtained by Tesla Model S battery. The battery pack is formed by 7,104 Lithium-ions modified Panasonic cells that use nickel-cobalt-aluminum as a cathode [6]. The energy that we can obtain from this cell is roughly  $265 \text{ Wh/kg}$ .

Their performances strictly depend on the material they are made of (Figure 3).

There are many energetic parameters that have to be taken into account when we discuss the energy storage concept. Here below, we will provide an example of the main energetic properties of the Li-ions battery, giving a range of values to have a main idea on their potentialities (Data have been taken from Panasonic Li-ions cells).

1. "Specific energy density: 100 to 250  $\text{Wh/kg}$  (360 to 900  $\text{kJ/kg}$ )"
2. "Volumetric energy density: 250 to 620  $\text{Wh/L}$  (900 to 2230  $\text{J/cm}^3$ )"



3. "Specific power density: 300 to 1500  $W/kg$  (at 20 seconds and 285  $Wh/L$ )"
4. Voltages: roughly 3.6  $V$  nominal voltage
5. Cycle life: 500-1500 cycles

Now, we will discuss Lithium-air batteries. They were proposed for the first time as a possible alternative to oil fuels in the 1970s but the interest has highly grown in the last five years. It is a possible technology for electrical energy storage, which could make highly performing electric vehicles more affordable [7].

Basically, the concept is pretty similar to Lithium-ions based batteries: they are mainly composed of the electrolyte, a cathode and a Lithium anode as well. Therefore, they seem to have the same architecture but the difference is that the metal cathode is substituted with a porous carbon-air cathode. The Lithium-air battery has an open-cell architecture and its design is much more simple when compared to Li-ions batteries, since it works with a gas that can flow through it. The positive aspect of the design is that the cathode is mainly composed by air; in this way, the energy that could be stored in the system is dramatically increased since the air cathode will not be part of the battery volume.

The goal that the 500 IBM project proposed could be probably reached with this technology; the idea was to get a battery that could make a car run for more than 500 miles, "which translates into a battery capacity of about 125  $kWh$  at an average use of 250  $Wh/mile$  for a standard family" [8].

Lithium is a super light material and the energy that we can get from its oxidation is 11,680  $Wh/kg$ , at the same order of magnitude of the gasoline specific energy, which is 13,000  $Wh/kg$ .

However, there is no possibility that any battery could effectively reach that value, since we have to take into account all of the possible losses that come from the charge, the discharge and every chemical reaction.

In addition, since the total efficiency of an EV is 90 % and the efficiency of an ICE car is 12 % only (from the engine to the wheels), the total energy that an electric vehicle requires as input is way lower and it has the same order of magnitude of the output wheel energy. In that way, to run a car that has the same power of a common combustion engine car, we will need a battery that is able to supply an energy of something around 1500-2000  $Wh/kg$ . We can now say that the lithium-ions based technology is not good at all since the maximum specific energy cannot overcome 300  $Wh/kg$ .

As we already said, the energy density of a Lithium-air battery is incredibly higher in respect to the previous Lithium-ions battery; it could reach a theoretical energy density of 5,200  $Wh/kg$  if the battery is working with pure oxygen, which is more than ten times the energy density we can get from every state-of-the-art lithium ion batteries [9].

However, the Li-air technology should be improved. It cannot substitute the Li-ions technology because of many challenges. In order to commercialize it, the battery should have a high efficiency for a high number of cycles. If we assume that the battery is charged 1-2 times a week and its life should be at least ten years, then the battery should have a stable efficiency for at least 500-1000 cycles. Unfortunately, the life of Li-air battery is still short and its efficiency dramatically decreases while we are using it. This is translated into a drop of the performances

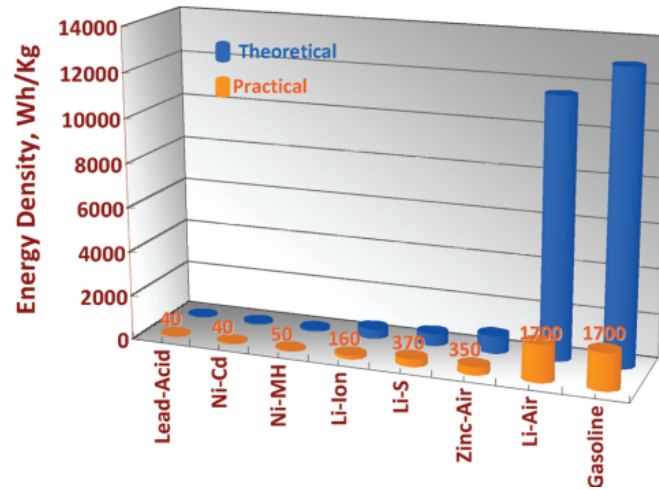


Figure 4: Theoretical and real energy densities of some kind of batteries compared to the gasoline energy density. Reprinted with permissions. ACS Publications [8]

and the decrease of its power. It has been shown that the capacity of a non-aqueous Lithium-air battery decreases to half only after 50 cycles (Figure 5) [10].

The problem does not affect the Lithium-ions based batteries, which instead present stable performances after 50 cycles (Figure 6) [11]. The issues that still have to be solved in order to improve the Lithium-air batteries performances involve:

1. The cathode: The products of the chemical reactions could be stuck into the pores of the carbon matrix of it
2. The anode: Since Lithium is very reactive, it could go through undesired chemical reactions during the charge and the discharge processes
3. The electrolyte: It should not react with any part of the system, especially with the anode

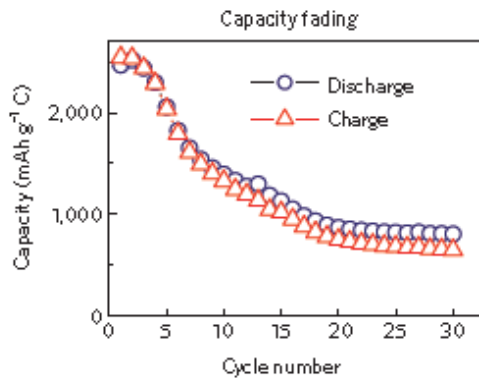


Figure 5: Example of stability of a Lithium-air battery from cycle to cycle. Reprinted with permissions. Nature. [10]

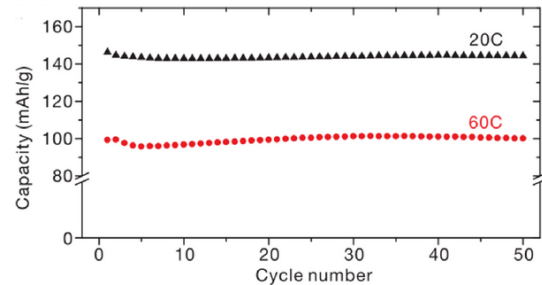


Figure 6: Example of stability of a Lithium-ions battery from cycle to cycle. Reprinted with permissions. Energy Science and Engineering, Wiley [11]

4. Impurities: Carbon dioxide or moisture can be part of the reactions
5. Catalyst: It could dramatically influence the performances of the reactions

We will thoroughly analyze every aspect we mentioned above and we will show in which way we tried to get higher performances of the cell in the next chapters.

## 1.2 Theory of the battery

Before focusing the attention on the Li-air battery, it is important to understand the principles of the energy storage of a battery. In this part of the introduction, we will briefly explain how a battery works and then we will analyze the properties of the Lithium in order to be able to understand why it is a suitable material for the energy storage.

A battery is a device that can convert chemical energy into electric energy: every reaction that happens in that system is spontaneous and the chemical process we can get energy from is straightforward.

To understand the way in which a battery works, we can first start analyzing the electro-galvanic open cell (Figure 7). It is a theoretical battery composed of two electrodes, which are made up of different materials. Every electrode is joined to a pole that is not connected to any circuit: this is the meaning of open circuit. In those conditions, the electrodes, which are immersed in the same electrolyte, start to lose positive metal ions in it because of their electromagnetic properties. Consequently, the non-dissolved metal (i.e. the electrode) assumes a negative charge in respect to the electrolyte, since some electrons will be free to stay on it. Since the electrodes are made up of different materials, the velocity by which they dissolve in the electrolyte is different. Therefore, the potential differential that the electrodes will reach in respect to the electrolyte, in steady-state condition (i.e. when the diffusion of the ions in the electrolyte is concluded), will be different too.

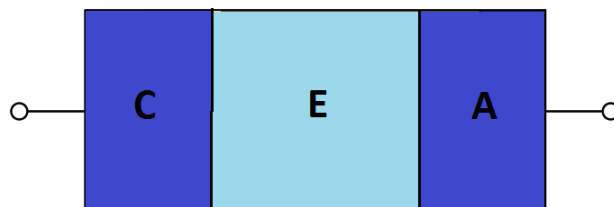


Figure 7: A schematic representation of a galvanic cell

That is the reason why if we connect the two poles with a conductive material, as a wire or a circuit, a current will start to flow, meaning electrons will start to move from one electrode to the other, due to the difference of potential. Such a system can be considered as a closed circuit, since electrons flow from the negative pole to the positive one. Meanwhile, a positive ions current, due to the concentration differential of positive charges lost by the electrodes, flows in the electrolyte, closing the circuit. The anode is the metal which oxides loosing positive ions and the cathode is the metal that reduces accepting ions.

The potential of the electro-galvanic cell can be easily determined by looking at the standard electrode potential data page [Table I]: It is a table in which we can find the potentials that every material will reach in steady-state conditions. Each materials potential is relative to

TABLE I: TABLE OF THE MAIN MATERIALS ELECTRO-CHEMICAL POTENTIALS

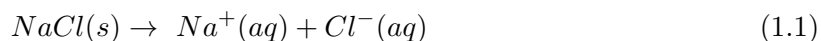
Electrode	Potential [V]
$Li^+(aq) + e^- \rightarrow Li(s)$	-3.04
$Ca^{2+} + 2e^- \rightarrow Ca(s)$	-2.76
$Na^+(aq) + 2e^- \rightarrow Na(s)$	-2.71
$Mg^{2+} + (aq) + 2e^- \rightarrow Mg(s)$	-2.38
$Fe^{2+} + (aq) + 2e^- \rightarrow Fe(s)$	-0.41
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00
$Cu^{2+} + (aq) + e^- \rightarrow Cu^+(aq)$	+0.16
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+0.80
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	+1.23

the hydrogen, which has been chosen as a reference point, with zero Volt potential. In this way, materials split into two main categories: these that can easily be reduced (gain electrons) will have a high potential, such as Oxygen (+1.23 V); and these that can be easily oxidized (lose electrons) will have a low potential, such as Li (-3.04 V). The first group of materials is called oxidant (or cathode) and the second one is called reducer (or anode). It is important to remember that every behavior is related to the reference system: that means if we compare two materials with a quite similar potentials, the material with the highest potential will be the cathode and the second one will be the anode as well.

Now, we will transition into the electrolyte. It has a crucial role in the working of the battery. It is the mean by which the ions can move and where the chemical reactions can happen. They are called second generation conductors since the current that can flow in it is made up of positive ions instead of electrons. When a difference of potential is applied to

any electrolyte, the positive ions that are dissolved in it will start to move from the anode to the cathode. The motion of the cations in the electrolyte will have an opposite direction in respect to the electrons that flows from one pole to the other: in such a way we can think that a negative current is flowing in the electrolyte in the opposite direction, closing the circuit we were discussing in the first portion.

The electrolytes are usually made of salts, acids or bases dissolved into a polar solution. The process is called solvation and the material that is dissolving loses its neutral charge dividing itself into anions and cations, even if the solution is still neutral. A typical example of a salt solvation is the solvation of the Sodium Chlorate into positive  $Na$  and negative  $Cl$ :



To give an example of a real battery and understand how it really works, we will start analyzing the Daniels battery. Basically, this battery is similar to the battery we discussed above: the only thing that is different is that a salt solid bridge is used to lead positive ions to move from the anode to the cathode. As noted in the Figure 8, the Copper electrode is the anode and the Zinc electrode is the cathode. Both the Copper and the Zinc will lose positive ions of  $Cu^{2+}$  and  $Zn^{2+}$  but with two different concentrations: it means there will be both a different concentration of charges in the electrolytes and a difference of potential between the electrodes. For that reason, a negative current in the wires and a positive current in the electrolyte will flow from the Copper anode to the Zinc cathode.



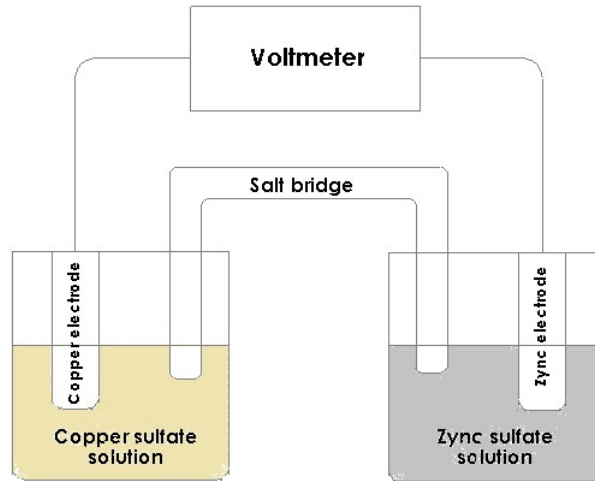


Figure 8: A schematic representation of a Daniel cell

The processes we explained above are the reactions that happen in the discharge process, which are the same for both chargeable and not-chargeable batteries. In general, we can find two kinds of battery: primary batteries (one-time use) and rechargeable (multiple-time use) batteries. The primary batteries we can find are D, C, AA, AAA and 9 Volt batteries. However, this thesis will focus its attention on rechargeable batteries, since they have suitable applications in the automotive field. They are made in such a way that they can be used more than one time, by restoring the electrode to the primary conditions by applying a voltage from an external source.

The charge process is exactly the reverse of the discharge: if we supply an electric charge from an external source by connecting it to the poles, we can charge the battery. In this way, we induce electrons to move from the cathode to the anode: this process is not spontaneous anymore since we are working against the electro-chemical nature of the electrodes. We will explain both charge and discharge processes in the following chapters by analyzing each reaction.

### 1.3 Chemical properties of Lithium

Before discussing the Lithium-Air battery, it is important to have a general overview of the chemical properties of the Lithium. Lithium is a solid metal, it is a member of the alkali elements and it is the least reactive. It has a single electron in the outer shell, which is very easy to remove by forming a positive ion  $Li^+$  that can rapidly react with negative ions, either organic or inorganic. Lithium has the smallest radius of all metals and, for that reason, it has a low atomic weight of 6.941 *gr/mol* with a density 1.5 times the water density only. In fact, it is considered a super light metal. The melting point of the Lithium is at 180.54 °C and it normal boils at 1317 °C.

Even if we consider Lithium as the least reactive between the alkali elements, we cannot say that it is an inert material. Lithium will not react with  $O_2$  or  $CO_2$  if there is no presence of water, i.e. if the mixture of gases is dry. On the contrary, only 10/15 ppm of water are sufficient to make it react with air,  $O_2$ ,  $N_2$  or  $CO_2$ , causing its corrosion and dissolution. In fact, water is a strong catalyst that allows the Lithium to react with many kinds of different gases. The most important Lithium-gases reactions have been reported in Table II.

TABLE II: TABLE OF THE MOST COMMON LITHIUM GASES REACTIONS [12]

Reactions
$2Li(c) + 1/2O_2(g) \rightarrow Li_2O(c)$
$2Li(c) + O_2(g) \rightarrow Li_2O_2(c)$
$2Li(c) + 1/2H_2(g) + 1/2O_2(g) \rightarrow LiOH(c)$
$Li(c) + 3/2H_2(g) + O_2(g) \rightarrow LiOH * H_2O(c)$
$2Li(c) + 3/2CO_2(g) \rightarrow Li_2CO_3(c) + 1/2C(c)$
$Li(c) + H_2O(l) \rightarrow LiOH(c) + 1/2H_2(g)$

Also, lithium is one of the only alkali metals that will react with nitrogen forming a nitride and with carbon dioxide forming the lithium carbonate. The temperature also plays an important role. No reactions will manifest at a temperature below  $160^\circ C$  for the Nitrogen and Oxygen. The same thing will happen at a temperature below  $300^\circ C$  for the  $CO_2$ . After the reactions, the Lithium surface is coated with a layer of lithium nitride, hydroxide, carbonate or oxide, depending on the kind of reaction it went through. Finally, Lithium will react also with water or vapor, forming lithium hydroxide and hydrogen gas [12].

## CHAPTER 2

### BACKGROUND INFORMATION AND THEORY

#### 2.1 The Lithium-air battery system design

We can start talking about the Lithium-air battery by getting a general overview of its structure as we already have done with the Daniels battery in the previous chapter. The architecture is similar to the theoretic Daniels battery and the structure is a way simpler if compared to the actual Li-ions battery.

Figure 10 shows the detailed structure of the battery. Starting from the top, the first component we can see is the cathode, which is composed of a gas diffusion layer (GDL). It is a porous carbon paper, which functions to let the oxygen penetrate into the battery through its porous matrix in order to react with the Lithium ions dissolved in the electrolyte. Usually, a layer of catalyst is coated on its surface in order to accelerate the kinetics of the reaction for both charge and discharge.

The second element is the glass fiber separator: it is a porous paper, usually wet by the electrolyte, which functions to allow the electrolyte to be in contact with the cathode and to prevent the anode from directly touching the cathode, leading to a short-circuit.

The third part is the anode, which is composed by a solid Lithium coin. The purity of the anode is 99.99 % and it has not been treated with any superficial layer.

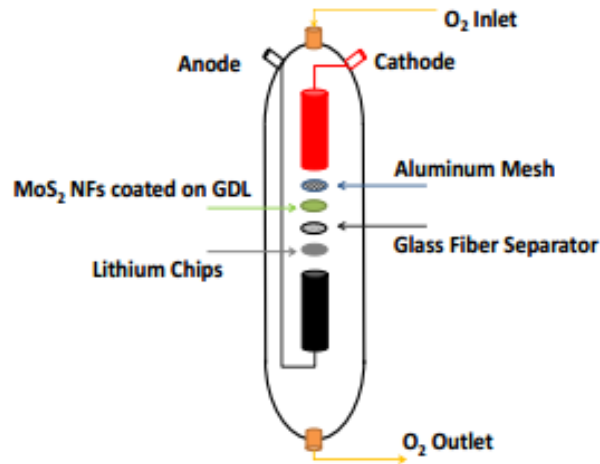


Figure 9: Scheme of the cell. Reprinted with permissions. Nature [33]

The whole system, after being assembled, is packed into a Swagelok-cell system in order to isolate the battery from the external environment and to recreate a sealed chamber in which air or any gas such as pure oxygen can be pressurized. There are two specific ways in which the system could work: the first one is static, i.e. there is no flow of gas inside the cell; the second one is dynamic, i.e. there is a continuous flow of gas, which leads the system to be open. The battery we are discussing in this work is of the first type.

The gas flows through the inlet valve as input and it flows out through a second valve as an output. Both the cathode and the anode are connected to two poles in order to be able to close the system and to measure the electrical performances of the battery.

As we can notice, the structure is quite simple but many aspects have to be taken into account.

From now on, we will discuss the feature of the Lithium-air battery.

## 2.2 Chemistry

In order to deeply understand how this new kind of battery works, we will start analyzing the chemical reactions that happen during the discharge and the charge processes. Before starting to talk about the chemistry, it is important to specify that the cathode chamber of the battery we are working with is filled with pure  $O_2$  only, instead of real air, considering most of the previous studies and breakthroughs have been made with pure Oxygen and we have quite a wide and certified literature on that topic. However, we will discuss real air and its reaction in the following chapters, since that topic will be part of this work.

Batteries are defined in different ways, but the most common classification focuses the attention on the electrolyte the battery is made of. In the literature, we find four kinds of batteries: aqueous electrolytic type, aprotic/non-aqueous electrolytic type, mixed/hybrid electrolytic type and solid-state electrolytic type [13]. The concept of these batteries is the same we already discussed, but the reactions involved and the final products are quite different.

In this work, we will analyze the aqueous and non-aqueous battery only, since most of the breakthroughs that have been done and most of the applications belong to those two prototypes. For both the electrolytes, the main reaction involved during the discharge is an oxide- reduction reaction. The mechanism involves Lithium, which has been dissolved in the electrolyte as  $Li^+$ , and the  $O_2$ , which has been reduced in  $O_2^-$  after having reacted with a free electron  $e^-$  in the

cathode side. All the reactions usually takes place in the cathode: lithium positive-ions move into the liquid solution leaving the anode and reaching the cathode, in order to react with the oxygen and form the precipitate as a final product.

The possible reactions involved in the oxide-reduction reaction (ORR) with a non-aqueous electrolyte could be:



In the first reaction (Equation 2.1) we can notice the irreversible reduction of the oxygen in order to form  $LiO_2$  as a sub-product by mean of one free electron. The  $LiO_2$  quickly either degrades into  $Li_2O_2$  (Equation 2.2) or it reacts with a Lithium ion (Equation 2.3) to form  $Li_2O_2$ . We can notice that in both cases, the final product is  $Li_2O_2$ , which has been demonstrated to be the main discharge product for a Lithium air battery. However, there is a possibility that  $Li_2O_2$  is reduced one more time to transform back into  $LiO_2$ , as shown in Equation 2.4 [7].

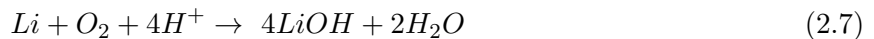
During the charge, the opposite reaction, i.e. the oxygen evolution reaction (OER) happens and the  $Li_2O_2$  will decompose in  $Li^+$ .



As we can notice, the  $LiO_2$  is an intermediate product during the  $O_2$  reduction. It is not the same with the oxygen evolution: the  $Li_2O_2$  jumps in one-step to the decomposition in  $Li^+$  and  $O_2$ , as we can read in Equation 2.5 . For this reason, we cannot say that the charge is exactly the theoretical reverse process of the discharge, since it has been demonstrated that the intermediate products are different. Moreover, we are ideally considering that the Lithium ions do not react with any impurities we can find in the electrolyte or in the cathode, like  $H_2O$ ,  $CO_2$ ,  $N_2$  or carbon. These elements are considered as unexpected elements that can participate to the reactions, modifying the path of the ORR and OER.

The reactions involved in the aqueous battery type are quite different since water is the main solvent: it is not inert and it participate to the ORR and OER processes. During the discharge, the oxygen is reduced by mean of a catalyst in  $OH^-$  at the cathode while Lithium ions are produced at the anode because of dissolution of Lithium in water.  $Li^+$  reacts with  $OH^-$  forming  $LiOH$ , which is soluble in water [7]. The pH of the solution does not influence the products even if the reactions involve different molecules, as it is shown in Equation 2.6 for basic electrolytes and in Equation 2.7 for acid electrolytes. Of course, the reactions we present here below have been shown in their short way, without going in deep in every single sub-reaction.





Lithium hydroxide quickly precipitates in  $LiOH \cdot H_2O$ , which has a low solubility in water (5.25 M at 25 °C). As for the non-aqueous electrolytes, during the charge  $O_2$  is generated by supplying energy from an external source and the lithium flows back to the anode.

The limitation of this kind of electrolytes is that the precipitate has a low solubility into the solvent and it saturates very fast limiting the energy density to no more than 170  $mAh/gr$  (less than a lithium-ion battery). Moreover, very expensive catalysts (like  $Pt$ ) are needed for both OER and ORR reactions in order to break or to re-generate the bonds of the oxygen: without them, the kinetic of the reaction will be very slow, decreasing the efficiency of the whole battery [7]. For all considerations, we can say that aqueous batteries have, at present, not suitable possibilities to substitute the actual Lithium-ions battery technology. This is the reason why, from now on, we will focus our attention on the non-aqueous batteries only.

### 2.3 Energy Considerations

Many experiments have been done in order to understand how much energy a system can provide from the ORR process, and how much energy an external source has to supply during the OER process. To understand the possible power of the battery, it could be useful to study the energy density of the active materials involved in the reactions.

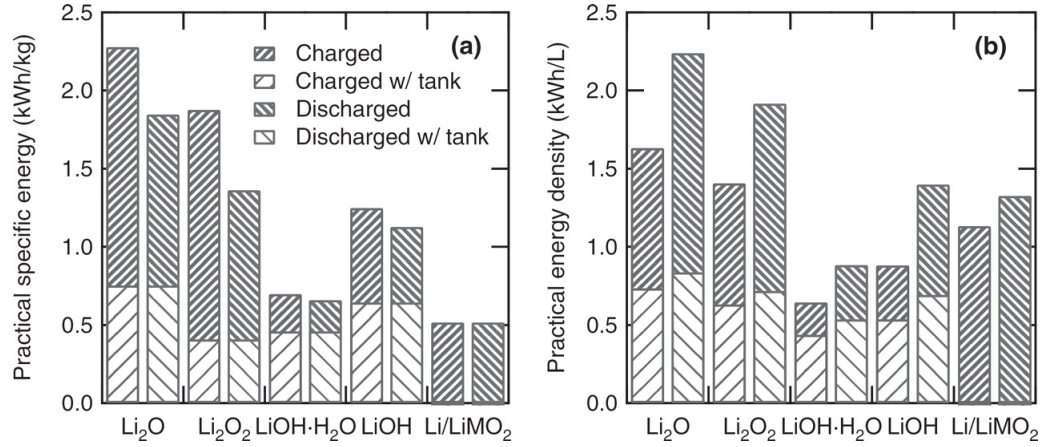


Figure 10: The main active materials specific energies and energy densities. Reprinted with permissions. ECS Materials [7]

The active materials are all the elements that come from the reaction such as  $\text{Li}_2\text{O}_2$ ,  $\text{LiO}_2$  or  $\text{LiOH}$  and  $\text{LiOH} \cdot \text{H}_2\text{O}$  (aqueous electrolytes) during discharge and  $\text{Li}$ ,  $\text{O}_2$  and  $\text{H}_2\text{O}$  during the charge. We have to be aware that the mass or the volume of the whole cell components are excluded from this calculation. As a matter of fact, it has been demonstrated that it is not possible to achieve something more than half of the pure active materials energy from the whole cell. So, to have a general idea on how much energy the battery could supply, we can study what potential energies the active materials can theoretically deliver.

Figure 10 shows the theoretical specific energies of some active materials involved into the processes. We can notice that the  $\text{Li}_2\text{O}_2$  has the highest specific energy in discharge with somewhere around  $5.5 \text{ kWh/kg}$ . That energy represents the maximum energy that the battery could

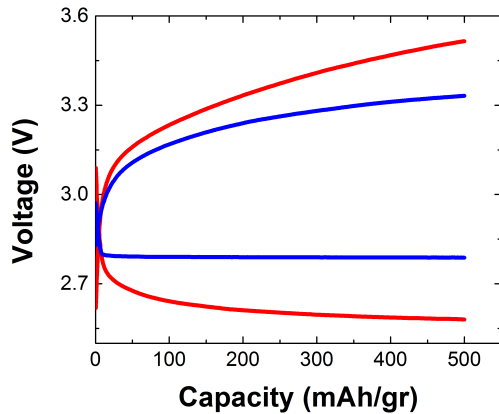


Figure 11: Example of polarization gap in a Lithium-air battery

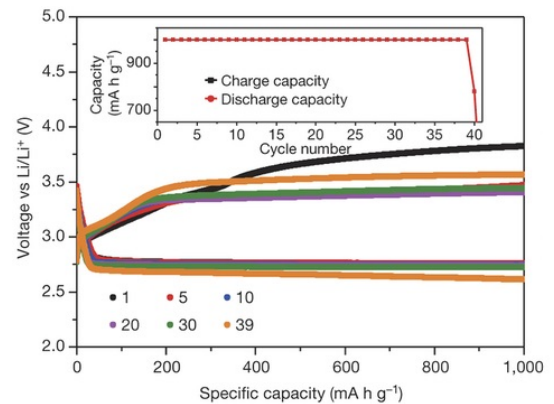


Figure 12: Example of cycle-ability in a Lithium-air battery. Reprinted with permissions. Nature Publishing Group [14]

deliver at the complete discharge, without considering any irreversibility or any additional resistance that comes from the real system. For that reason,  $LiO_2$  would be the best final product we can get from the discharge. Moreover, the specific energy required to decompose both the  $LiO_2$  and  $Li_2O_2$  is the same ( $11.5 \text{ kWh/kg}$ ): this is translated into a higher efficiency of the battery that works with  $LiO_2$  as the main product. Unfortunately, it has been demonstrated that this product cannot be obtained because  $Li_2O_2$  forms more readily [7], but recent discoveries showed that there is a possibility to get  $LiO_2$  as the main discharge product; therefore, enhancing the performances of the battery [14].

An important electro-chemical phenomenon we should analyze is the complete reversibility of charge and discharge processes, i.e. the efficiency of the battery. There is a typical voltage gap between the charge and the discharge profiles that cannot be avoided (Figure 11). The fact

is due to both cell-system impedance and to the different mechanisms of reactions that happen during the charge and the discharge. The gap has to be considered as an irreversible loss: we will always get a higher voltage during charge and a lower voltage in discharge. Achieving the lowest gap voltage will lead to the highest efficiency battery. The main idea is that we want to get from the battery the same energy we previously spent by charging it, and the difference of the two voltages will lead to irreversible energy lost. The gap represents a hysteresis effect and it cannot be avoided at all. Even though we cannot delete it completely, one of the main goals of the research is to minimize it. The voltage difference is related to many aspects, such as type of electrolyte, cathode, current rate, size of the electrodes etc. We will discuss in depth this aspect further on.

In order to be able to insert the battery in the market we have to guarantee it has a long life term. In fact, it should work properly for quite a long period; this means it should be cycled for thousands of cycles without changing its electrical behaviors. This cycle-ability is directly related to the reversibility of the charge and the discharge processes, which strictly depend on the anode, cathode and electrolyte. In fact, if the processes would be completely reversible, the initial and final point of the reactions will match forever and the battery could theoretically work in the same way forever. The cycle-ability is also influenced by other factors such as the anode or the cathode degradation: it means that even if the reactions have a good reversibility, the battery could reduce its performances because of other problems not related to the electro-chemistry field, such as mechanical degradation, increase of the temperature, decrease of the transport velocity etc. The main effect of these aspects is a decreasing of the

electrical performances of the battery, i.e. an increase of the potential gap. As a matter of fact, after cycling the battery for many times, the performance will not be the same as the first cycle and the efficiency will start to decrease from cycle to cycle, as we can notice in Figure 12.

The biggest goal of the research is to minimize the potential gap by increasing the reversibility of the processes, leading the battery to have a higher performance and a longer life.

## **2.4 Electrolyte**

The electrolyte represents a fundamental parameter for both the reversibility of the charge-discharge process and for the cycle-ability of the battery . The most suitable electrolyte we should use is made of a solvent: that does not react with Lithium or intermediate products, that does not reduce if it is in contact with the oxygen and that does not degrade during its life time. The challenge is to find a good inert electrolyte, which would improve life cycle quality of the Lithium-Air battery.

The properties that a good electrolyte should have are: high ionic conductivity, good oxidation potential, good stability with lithium electrode, high electrical window, low vapor pressure, high lithium salt solubility and high boiling point.

As we mentioned before, we divide the electrolytes into aqueous and non-aqueous type. The aqueous type is not practical for the battery unless we find a way to protect the anode from parasitic degradation [15] and we find a way to increase the solubility of the products.

Instead, the non-aqueous type has been deeply studied and we will cover only that topic in this thesis. Currently, we can divide the non-aqueous electrolytes into three main categories, based on the type of solvent: organic carbonate based, ether based and ionic liquid.

The organic carbonate based electrolytes are "usually made of propylene carbonate, ethylene carbonate, diethyl carbonate or dimethyl carbonate" [16]. These electrolytes have many suitable applications since they have a low volatility and they have a high Lithium ions conductivity without chemically attacking the metal anode. Moreover, carbonate solvents usually form a solid electrolyte layer (SEI) on the Lithium anode, protecting and stabilizing it. In this way, the battery design will be simplified since we do not need to use any membrane to separate the electrolyte from the anode, since we do not need to protect the anode from the chemical attack of the electrolyte. Propylene carbonate (PC) is the most common solvent: it can guarantee a good solubility for both Oxygen and Lithium, good viscosity of the electrolyte and proper polarity. However, it has been demonstrated that the carbon reacts with the Lithium ions and it decomposes in  $Li_2CO_3$  instead of  $Li_2O_2$  [16]. This could be a problem because the battery will lose energy density during the discharge process. The same problem happens in the charge process: it has been shown that the main product during the charge is  $CO_2$  instead of labeled  $O_2$ . In this way, the reversibility of the charge and discharge process is disrupted, since two different products form, and a performing cycle-ability of the battery cannot be guaranteed anymore.

The Ether based electrolytes are interesting since they are very stable with the Lithium anode, i.e. they can guarantee a long life of the anode. Moreover, they are inexpensive and they have a low volatility and they are not dangerous. Unfortunately, Ether based electrolytes are affected by the same problem as the organic carbonate based electrolyte with respect to the reversibility of the processes. It is true that Ether electrolytes do not react with the Lithium

anode but, on the other hand, they react with the products that come from the reactions. As a matter of fact, it has been noticed that after five cycles of charge and discharge, the presence of  $Li_2O_2$  in the cathode at the discharge is almost null and it is replaced by the products of the decomposition of the electrolyte, such as  $Li_2CO_3$ ,  $HCO_2Li$  and  $CH_3CO_2Li$ .

For that reason, those two kinds of electrolyte are suitable to lead the battery to a long cycle life. This fact diverts the research towards the ionic-liquid based electrolytes (ILs). They show the same properties we discussed above, like high solubility of Lithium and Oxygen, high potential in discharge oxidation and very high capacity in discharge such as  $5000\text{ mAh/gr}$  [16]. The only issue of these new kinds of electrolytes are that it is not that easy to have both good electro-chemical stability and low viscosity of the fluid. This fact could lead the battery to very high losses because of ion transportation issues. Much research is still going on about that topic, but the scientific world is starting to think that the ionic-liquid based electrolyte could be a good way to improve the quality of the battery in order to get batteries with very high performances. We will cover this topic in depth in the following chapter, since the battery we will analyze works with this kind of innovative electrolyte.

## 2.5 Air Cathode

The cathode is an essential part of the battery since most of the reactions happens in that side. The first task of the cathode is to guarantee the flow of  $O_2$  in order to reduce and to react with the  $Li^+$ . The easiest way to do that is to use a cathode that is both solid and it has a high porosity. For that reason, the main part of the air cathode is a porous matrix made of carbon. Usually, the matrix is designed in order to have a high conductivity in order to

decrease the over potential and a high wettability, because it has to guarantee the infiltration of the electrolyte into the matrix. Another important property of the matrix is to avoid the penetration of  $CO_2$  and  $H_2O$  from the external environment, since we do not want impurities involved in the ORR or OER processes and since we want to protect the Lithium anode from those reactive elements.

Many materials have been investigated in order to get a proper cathode, such as Nanotubes, graphene and mesoporous carbon: the research is centered on the uniformity of the pores, which plays a crucial role in the electro-chemical reactions. If the pores are too little, like micro-pores, the precipitate of  $Li_2O_2$  will suddenly block the entrances and it will disturb the reactions [13]. Therefore, working with bigger pores could be useful and beneficial to store discharge products. A good trade-off between pores volumes and pores diameters could be the key point to get a high energy density. The surface area of the cathode is also important since it facilitates the electro-chemical precipitation of the Lithium oxide. In fact, if the surface area is higher then it will become easier to form oxides, thus increasing the specific capacity of the battery.

Carbon is not considered to be an inert material so it can be part of the reactions due to its reactive properties. The oxidation of the carbon represents a huge problem for the time-life stability and cycle-ability of the battery. The electrode literally deteriorates during the OER reaction resulting in a loss of the electrochemical active surface due to its corrosion. It has been proven that the production of the  $Li_2O_2$  is not the only cause of the carbon degradation and that we can decrease the phenomena by charging the battery at a low voltage [17]. Another



way to decrease degradation is to use a catalyst. It has been noted that we can protect the cathode by coating a catalyst on its surface. As already stated, one of the main rules of using the catalyst is to protect the cathode from its poisoning, which will lead to a definite decrease of electric performances of the battery.

## 2.6 Lithium Anode

The Lithium material has been chosen to be the anode of the battery because its high electropositivity is  $-3.04$  V. Moreover, as previously stated, Lithium is one of the lightest metal found in nature with an atomic weight of  $6.941$  *gr/mol*. Those two important characteristics lead the Lithium to have many suitable applications in the energy battery storage. Unfortunately, many problems need to be resolved before being able to commercialize this new kind of battery.

First of all, Lithium is a very reactive element, especially with the electrolyte. It reacts violently with the electrolyte deteriorating within. Usually, as soon as the reactions start, a solid electrolyte surface (SEI) starts to cover the external surface of the anode with a Multi-layer structure. The SEI can either have a positive or negative effect. It could be useful due to the fact that it protects the metal surface from its degradation, but it could also be dangerous because it causes the battery to gradually lose capacity during its whole life. The main cause of the loss of capacity is the heterogeneous distribution of the layers on the anode surface. This causes a non-uniform distribution of the currents, which leads to the formation of dendritic structures that can grow, thus increasing the surface of the anode. Moreover, since the layer is not conductive, it will increase the resistance of the system, i.e. the over potential during charge and discharge. As a matter of fact, the SEI usually requires a noticeable potential energy in

order to transfer ions from the anode to the electrolyte, decreasing both the efficiency and the energy stored in the battery.

When the dendritic structure is so big to touch the cathode side, it generates a short circuit and the battery fails. Sometimes, instead of short circuit, the layer can crack or be broken during the charge and discharge processes. This is even more dangerous since the battery can literally explode or burn because the current density at the edge of the broken layers could be so high that it ignites the electrolyte. Even if the discharge process usually tends to smooth the surface of the anode, since we have the degradation of the material, a layer of SEI will still remain and it will accumulate, growing up from cycle to cycle. It has been noted that the problem is drastically increased if the current rate, during the charge process, is higher. This causes the short circuit to occur earlier and the life of the battery will be much shorter [13].

Many analyses have been made in order to understand the real structure of the SEI and it has been found that two principal layers compose it. The first is made up by inorganic elements such as  $Li_2CO_3$  or elements that come from the reaction of Lithium with external elements such as  $CO_2$ ,  $H_2O$ ,  $N_2$ . The second layer is usually made up of HC, electrolytes and lithium metal [18].

Through the years, many ways to reduce the excessively growth of the SEI layer have been analyzed. The simplest idea (it does not mean that it is the easiest) is to find an electrolyte that does not react with the anode at all. The challenge is very daunting since the Lithium is very reactive and to find an inert electrolyte that respects all the characteristics required seems very difficult. Another technique that is a little bit more complex could be to recreate some

layers in between the electrode and the electrolyte in such a way to eliminate the problem of dendrites formation. We could also use some special membrane that allows only the  $Li^+$  ions to flow in both directions in order to protect the anode from the electrolyte and every possible reactions.

## 2.7 Catalyst

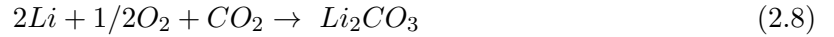
The catalyst has a fundamental role in the Li-air battery electrical performances. It is essential and it gives two important benefits to the battery. First, it can dramatically improve the performance of the ORR and OER kinetics leading to a higher capacity and, secondly, it is useful to improve the cycle life [19]. Moreover, the catalyst has the role to minimize the potentiometric gap between the charge and the discharge processes. If the catalyst is able to enhance the properties of the battery, it will make the system more complex. The use of the catalyst causes the battery to have stability issues, since charge and discharge process dynamics are quite different. For that reason, many studies have been conducted in order to get a bifunctional catalyst [7]. We want to work with a catalyst that provides beneficial effects on both ORR and OER. As regards to the type of catalyst, many materials have been tested, such as metals or oxides, but the right choice is directly related to the kind of electrolyte we are working with.

## 2.8 Carbon dioxide as impurity

The impurities should be considered when we discuss the performance of the battery, since they could be involved in the reactions. The more the impurity is reactive, the more will be part either of the ORR or the OER processes. In this section we will examine what should

be the issues if we involve  $CO_2$  in the reactions. We are particularly interested in  $CO_2$  first because it can actively react with  $Li$  or  $O_2^-$  and than because we can easily find it in nature in a quite important quantity.

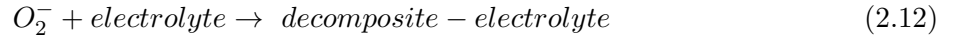
The main product of the reaction between Lithium, carbon dioxide and oxygen is Lithium Carbonite –  $Li_2CO_3$  – as shown in Equation 2.8. The energy associated to the reaction is  $\Delta_f G^\circ(Li_2CO_3) = -135.30 kcal/mol/Li$ , which is lower than the energy formation of  $Li_2O_2$  which is  $\Delta_f G^\circ(Li_2O_2) = -68.26 kcal/mol/Li$ . That is the reason why there is always a chemical force that drives the  $Li_2O_2$  to convert in  $Li_2CO_3$  if we are working in presence of  $CO_2$  [20].



Equation 2.8 is a short way to show the reactions during the discharge of the battery. Going in deep in the whole reaction processes, we can see that the first reaction involved is an oxygen reduction, i.e. the oxygen reacts with a free  $e^-$  on the cathode (Equation 2.9).



After that it starts the Initial Complex Formation (ICF) in which the  $O_2^-$  reacts with different elements such as  $CO_2$ ,  $Li$  or the electrolyte. For each case, the final intermediate product will be different and with different thermodynamic status.



The last step of the process will lead to the final products. If the  $O_2^-$  reacts with the  $Li$  (Equation 2.10), the process we already explained in the section (Chemistry) will happen. The most common product of that reaction will be  $Li_2O_2$  and the reaction of Equation 2.1 will be most favored because of its low energy, regardless the electrolyte. If the  $O_2^-$  has reacted with the  $CO_2$  (Equation 2.11),  $Li_2CO_3$  will be the main product. The process is quite complex and it will involve many intermediate products. Moreover, the process strictly depends on the electrolyte we are working with and for that reason we will not cover this topic. The important thing is that we have to be aware that some  $CO_2$  is introduced in the gas mixture, that set of the chemical reactions will complete different. Therefore, this fact will dramatically influence the electrical performances of the battery.

## CHAPTER 3

### EXPERIMENTAL SETUP

#### 3.1 Assembling of the battery

In this section we will describe how the battery is prepared and assembled, going in detail on every element that composes the system.

The battery is composed of:

1. A top cover made of stainless steel
2. A stainless steel spring and chip with a dimension of  $7/6''$ . They are used in order to improve the electric connection between the battery and the cell
3. A  $MoS_2$  coated cathode with a dimension of  $7/6''$
4. A glass fiber separator. It has two important functions: the first one is to allow the electrolyte to be inserted between the cathode and the anode, the second one is to avoid the cathode directly touching the anode, causing a short-circuit
5. The electrolyte, which is spread on the glass fiber separator by means of a pipette. In order to have the best performances, a good homogeneity of the solution on the paper has to be guaranteed
6. The anode, composed by a chip of lithium with a dimension of  $7/6''$
7. A bottom cover made of stainless steel

The battery is assembled in the glove box, which is a special chamber that works with a very low pressure (almost below 0.01 bar) in which the percentages of contamination like  $O_2$  or  $H_2O$  are close to zero (never more than 0.5 ppm). The box is filled with a small percentage of Argon in order to push out all the other possible contaminants. Argon does not represent a problem since it is an inert material and it does not react with any element of the battery.

The reason why we assemble the battery in the glove box is that we do not want either the lithium chip or the electrolyte reacting with the oxygen or the moisture that could be present in the air. To prevent any contamination from the external environment, an Air-lock chamber is used to introduce the elements inside the glove box. Obviously, the doors must not be open at the same time in order to avoid any undesired element from getting in.

After having assembled the battery, the sample is locked into the Swagelok-type cell: it is an hermetic cell that allows the system to work with a pressurized gas. The Swagelok-cell is made up of two stainless steel disks and a plastic ring, which is used to recreate a closed chamber that will be filled with gas through a Swagelok valve. Of course, the cathode side must be on the top of the cell since it must be directly in contact with the oxygen chamber. We have to be sure that the cell is locked in the right way and that the inlet and outlet valves are closed before taking out the cell from the glove box, in order to avoid that some external air from getting into the cell.

From now on, we will describe every part of the battery and we will show the process we used to prepare it.

### 3.2 Preparation of the Electrolyte

Aprotic ionic liquids (ILs) were thoroughly studied and they could replace the traditional organic or inorganic electrolytes because of their properties. Basically, ionic liquids are mixtures of different salts which are liquid at a room temperature. This is very unusual because ionic bonds are very strong and they should lead to a solid material at a low temperature. We can consider ILs similar to a strong acid that can dissociate into ions. The ionic liquids are usually made of asymmetric organic cations bonded with inorganic anions.

The ILs we are working with is made of an organic cation  $EMIM^+$  (1-ethyl-3-methylimidazolium) and a inorganic anion  $BF_4^-$  (Tetrafluoroborate). The main properties that lead the  $EMIMBF_4$  to be a suitable electrolyte for batteries applications are [21]:

1. Low viscosity: it plays an important role on the diffusion and transport of the elements dissolved in it
2. High conductivity: it basically depends on how the cations can move through the electrolyte. In general the ILs have a conductivity higher than  $10^{-5}$  -  $10^{-7}$   $S/m$  [21]
3. Fast ions mobility during redox reactions ( $10^{-14}$   $m^2/Vs$ ) [21]
4. High Lithium ions solubility
5. Large electro-chemical window: it represents the electro-chemical stability of the electrolyte against the oxidation process. The higher the window, the highest the voltage gap in which the electrolyte does not oxides or reduces, i.e. the electrolyte is stable. The limit of the window will represent the limit in which the ions dissolved into the electrolyte start



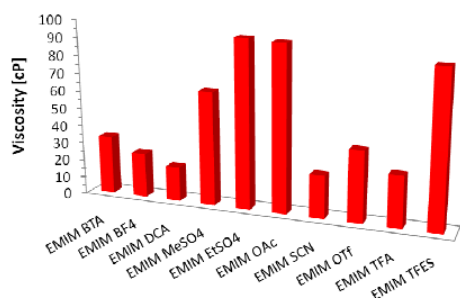


Figure 13: Viscosity of different ILs. Reprinted with permissions. IOLITEC

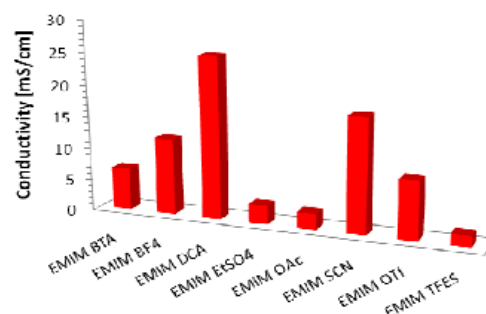


Figure 14: Conductivity of different ILs. Reprinted with permissions. IOLITEC

or end to decompose. Moreover, it has been demonstrated that the window is pretty sensible to the impurities that are present in the solvent: as we can imagine, contamination will lower the electro-chemical stability of the ILs

Figure 13 reports some examples of viscosity of the most common ionic liquids. We can see that the viscosity of the  $EMIMBF_4$  is of 25 *cP*. Instead, Figure 14 shows the conductivity of the most common ILs. In this case, the conductivity of  $EMIMBF_4$  is of 12.5 *mS/cm*. The value of the viscosity is not the lowest if compared to the other ILs, and the value of the conductivity is not the highest either. However, we cannot forget that we need both conductivity and viscosity to get the highest properties, and  $EMIMBF_4$  could be a good trade-off since it shows a low viscosity, a high conductivity and a low price.

The structure of the cation  $EMIM^+$  is a five-membered ring composed of three carbons and two nitrogen atoms. Meanwhile, the structure of the Tetrafluoroborate has a tetraedric

shape with the Bore in the middle. The anion is very sensible to the hydrolysis: it means that if there is some water in the electrolyte its properties will strongly decrease [22].

To get a system with a very high performance, it is also possible to add some salts to the solvent in order to tune up its properties, like conductivity or stability. For Lithium-ions or Lithium-air batteries, it has been demonstrated that we can get higher properties if we mix Lithium salts with the solvent. Salts like  $LiCLO_4$ ,  $LiBF_4$  or  $LiPF_6$  have been analyzed through the last years. The properties that a lithium salt should have are: high solubility in order to make the motion of ions  $Li^+$  faster, stability at a certain potential voltage and high stability with the solvent, in order to not originate any unexpected product [23].

Recently, it has been demonstrated that  $LiTFSI$ , or better known as Lithium imide salt, can improve the battery performance even more [22]. The lithium-containing electrolyte will thus be called  $LiTFSI/EMIMBF_4$ . It has been demonstrated that the ionic conductivity of the ILs dramatically increases if  $LiTFSI$  is added [24].

The way in which we prepare the solution is simple. We mix the salt with the ionic liquid in a Becker. The proportion we want to obtain is 10 % of the weight of the salt dissolved in 1 liter of ionic liquid (0.1 M). The calculation is straightforward since we know that the molecular weight of the  $LiTFSI$  is 287.09  $g/mol$ . By applying the Equation 3.1, we can get the required weight of the salt we need to mix the solvent.

$$W_{salt}[gr] = 0.1 * \left(1 \frac{mol}{l}\right) * \left(287.09 \frac{gr}{mol}\right) * V_{ionliquid}(l) \quad (3.1)$$

Several of the experiments we will show in the next chapter are related to the pure IL as electrolyte. Other results have been obtained using an organic-based electrolyte.

*DMSO*, or better known as Dimethyl Sulfoxide, is an organosulfur compound with  $(CH_3)_2SO$  as a chemical structure. Its main properties are high melting point and good miscibility in a wide range of polar and nonpolar compounds. It has been demonstrated that *DMSO*-based electrolyte can easily stabilize the products and the intermediates of the oxygen reduction reaction and, for that reason, it could lead the battery to a high quotient efficiency [25].

Theoretically, it has been demonstrated that pure *DMSO* could be a good electrolyte because it leads to a reversible ORR and OER processes. On the other hand, it is also well known that *DMSO* reacts with the intermediate products of *Li* and  $O_2$  that are generated into the reactions. It has been shown that *DMSO* is not stable since it reacts with  $Li_2O_2$  giving *LiOH* as a product [26]. That product is not good for the reaction because its formation is not reversible and it will be stuck in the cathode pores, dramatically decreasing the cycle-life of the battery. Moreover, it has been demonstrated that an additional undesired SEI substrate will be formed on the anode surface if the electrolyte is pure *DMSO*. This fact will decrease the life of the battery even more [27].

Mixing an organic electrolyte, such as *DMSO*, with an ionic liquid has shown interesting improvements of the battery. The addition of IL gives an enhanced result of the performances such as: reversibility of the reactions, conductivity and lower voltage in charge. Mixed electrolytes could thus be a good trade-off to increase significantly the electric properties of the

battery. It has been shown that the ORR performs a much higher current density if compared to pure *DMSO* [28].

The preparation of this electrolyte is easy as well. We mixed the IL with the *DMSO* in a Becker, simply calculating the right proportions in volumes. After mixing the two solvents, we saturated the solution with the *LiTFSI*. The weight of the salt that we have to mix with the solution is calculated with the same relation we discussed above, i.e. Equation 3.1.

### **3.3 Preparation of the Cathode**

The cathode has a crucial role in the performances of the battery since every reaction happens in that place, and since part of the resistance that causes the potential gap between charge and discharge belongs to it. The resistance is mainly caused by three parameters: the electronic conductivity (related to the material electronic properties we are working with), the thickness, and the widths of the channels [29].

The gas diffusion layer (GDL), a macro-porous black matrix of carbon that is used in many energy storage systems, is the cathode. The GDL is made up of 90 % carbon and 10 % dry Teflon. The GDL is located in-between the liquid electrolyte and the gas phase reactants: in this way, three layers made of three different phases compose the gas diffusion electrode (GDE), which consists of the liquid phase, the carbon paper and the gas phase [30]. Moreover, the GDL is usually treated in such a way to make it hydro-repellent, in order to avoid some water passing through the matrix. In addition, we coat the GDL surface with a catalyst, in order to improve its performances. Therefore, we can say that the three layers the hydro-repellent, the catalyst

and the carbon-diffusion layer compose the GDL. In summary, we are working with a membrane composed by three different layers in a system made up of three different phases.

The main function of the GDL is to make the liquid electrolyte react with the gas on the cathode side. Every pore has to be considered as a channel in which the gas flows in order to reach the electrolyte and start the reactions. The electrolyte tends to fill the pores because of the capillarity effect, but its surface tension will avoid the flow of the liquid through the channels. In this way, the electrolyte will cover the whole surface of the GDE without completely filling it. The GDL will start to work in a proper way when the pressure in the gas chamber will be a little higher than the atmospheric pressure, in order to have a unidirectional motion of  $O_2$  particles from the gas chamber through the carbon layer. Also, the pressure is required in order to avoid penetrating the liquid completely in the GDL. If the carbon electrode is too wet, gas will not be allowed to flow from one side to the other, and so the reactions will not happen. On the other hand, we have to avoid working with too high pressure. This is because we will push the electrolyte completely out from the GDL without any reaction either.

One of the main problems of the GDE is that it stops working properly when the precipitates that come from the reactions between lithium and oxygen during the discharge block the pores. Even if we already said that the processes that involve  $Li_2O_2$  are quite reversible, after charging and discharging the battery for several times, some particles will not decompose again in  $Li$  and  $O_2$  and, therefore, some  $Li_2O_2$  will remain on the GDL. Those products accumulate in the carbon layer decreasing the cycle life of the battery. Therefore, the porosity of the GDL plays a fundamental role in the battery functioning.

It is very important to find a tradeoff between the porosity and the dimension of the pores. The higher is the porosity, the more the gas can diffuse through the carbon paper. Moreover, it has been demonstrated that the capacity of the GDE increases linearly with the dimensions of the pores [30]: if the pores are too little, the area cannot be utilized for the O<sub>2</sub> reduction since the Lithium oxide will occupy the spot, disturbing the mass transfer.

### 3.4 Preparation of the Catalyst

#### 3.4.1 Catalyst properties

$MoS_2$ , or better-called Molybdenum Disulfide or Molybdenite, is a layered transition metal that has a structure very similar to graphene. It has a hexagonal crystalline structure and it is usually easy to find it in nature with a 2D geometry. A layer of molybdenum ions and a layer of sulfur ions, sandwiched between each other, compose its structure [31]. Figure 15 shows its configuration: every Molybdenum atom is covalently bonded to six sulfur atoms, and each sulfur atom is covalently bonded with three Molybdenum atoms in total. The sulfur ion layers are strongly bonded to the molybdenum ion layers, but the configuration is not the same with the nearest sulfur ion layers. This is the reason why we consider molybdenite as a soft material because the bonds between the two adjacent sulfur ion layers exist due to the Van Der Waals forces [32].

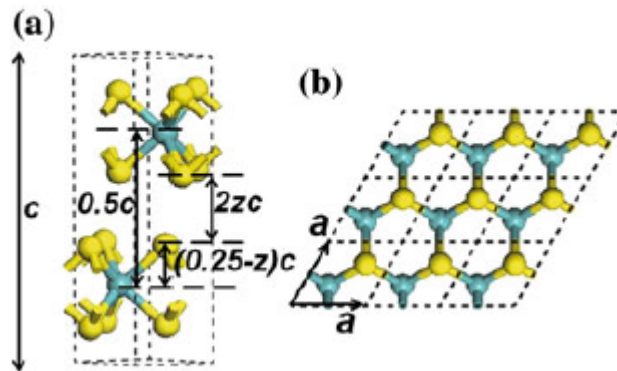


Figure 15: Chemical structure of the  $MoS_2$ . Reprinted with permissions. Elsevier. [31]

This kind of weak bond enables the exfoliation of  $MoS_2$  in single flakes. Recently,  $MoS_2$  has been exfoliated in  $S - Mo - S$  mono-layer: in those conditions, it has been noticed that the material shows particular electric properties, suitable for many technological applications.

The price of Molybdenum Disulfide is quite lower if compared to the most common catalysts: an ounce of  $MoS_2$  costs \$ 6.99; instead, a ounce of Platinum costs \$ 954.40 and a pound of gold costs \$ 1,218.90. Also, if we compare the  $MoS_2$  Nano-flakes with the materials we previously cited, we can notice that it leads to a noticeable improvement of the kinetics of the reactions such as ORR and OER.

Every result that will be shown in this section has been analyzed with a  $MoS_2$  NFs in a standard three-electrode electro-chemical cell where pure IL or 25% of IL in  $DMSO$  saturated with 0.1 M of  $LiTFSI$  are used as electrolytes.



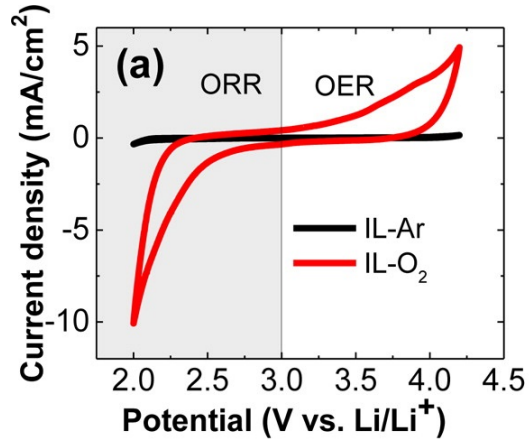


Figure 16: Cyclic-Voltammetry test using  $MoS_2$  as a catalyst with Oxygen and Argon. Reprinted with permissions. Nature. [33]

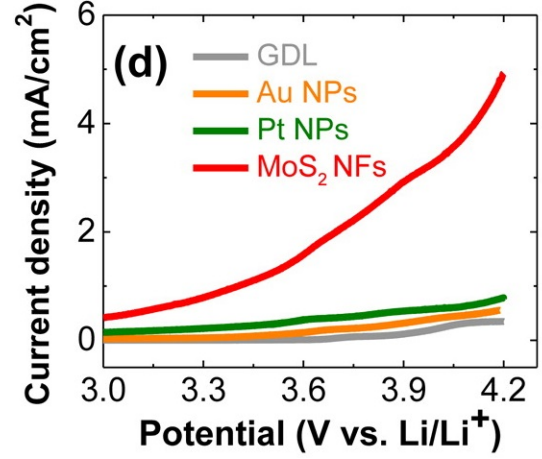


Figure 17: Current densities in the cathode led by different catalysts. Reprinted with permissions. Nature. [33]

Figure 16 shows cyclic voltammetry test of  $MoS_2$  as catalysts with both  $O_2$  and  $Ar$  environment: in  $O_2$  environment  $MoS_2$  shows a current density peak of  $10.5 \text{ mA/cm}^2$  at  $2.0 \text{ V}$  in ORR and  $5.04 \text{ mA/cm}^2$  at  $4.2 \text{ V}$  in OER [33].

Instead, Figure 17 compares the performances obtained with  $MoS_2$  to Au and Pt catalysts. Surprisingly, we can notice that the current density obtained with the GDL coated with  $MoS_2$  is much higher than the current obtained with the GDL that has been previously coated with Gold or Platinum. The highest current is in the range of  $3.0 \text{ V}$  up to  $4.2 \text{ V}$  and the peak for  $MoS_2$  is  $5 \text{ mA/cm}^2$ , at least five times more than the current densities obtained with the other catalysts [33].

### 3.4.2 Exfoliation

Since it has been demonstrated that  $MoS_2$  shows its best electrical properties when it is in Nano-flakes form, we used liquid exfoliation to get 2D single-layered Nano-sheets. The technique we applied is the liquid-phase exfoliation (LPE). It is a new versatile method, since it is easily scalable and it can be applied with different materials such as  $MoS_2$ ,  $WSe_2$ ,  $NbSe_2$  or Graphene. The LPE effect is due to the mechanical exfoliation. The exfoliation takes place in a liquid environment by means of ultrasound waves that extract individual layers from the starting material by means of a vibrating sonotrode.

Three steps compose the process: dispersion of  $MoS_2$  in the solvent, exfoliation and purification [34].

In the first step, the  $MoS_2$  powder is mixed into a liquid solvent. We chose to work with 2-Propylen (IPA) as solvent. In this step,  $MoS_2$  particles start to diffuse in the solvent due to the concentration differential and spread in order to obtain an homogeneous solution.

The exfoliation of the bulk of  $MoS_2$  belongs to the second step. The exfoliation of the material is due to shear stresses and cavitation that are produced by the Ultra-sonication process. The pressure fluctuations produce bubbles and voids and, finally, their bursts and implosions cause the exfoliation of the material.

The third step involves the solvent: it works as a balance element by reducing the contact surface area between the particles, minimizing the inter-facial tensions. In fact, if the particles are in contact with each other in more points, their tendency to be bonded will be higher. Therefore, a solvent with a high surface tension will be essential to improve the dispersion of

layers. Moreover, the London interactions between solvent and sulfur ions will be weaker than the previous Van Der Waals bonds: this fact will increase the dispersion of the solute layers in the solution. The higher the surface tension of the solvent, the higher the effect.

However, it is crucial that we do not coat too many impurities (as the solvent) on the cathode. This means that the solvent should have a low boiling point in order to rapidly evaporate; thus, we are not free to choose the solvent with the highest surface tension we can find in nature.

The characterization has a crucial role in the liquid exfoliation process. It is a way to measure how many single layers of  $MoS_2$  we get from it. The main method to determine the quantity of single-layered flakes that we can get from the exfoliation is defined by the ratio between the number of the single-layered of  $MoS_2$  and the total number of  $MoS_2$  flakes. For instance, the ratio between the mass of single-layered flakes that have been dispersed and the total mass of the dispersed flakes. In particular, we can get the average concentration of the dispersed  $MoS_2$  flakes by means of the optical absorption spectroscopy method and we can get the total number of the exfoliated  $MoS_2$  layer flakes by using the transmission electron microscopy or the atomic force microscopy techniques [34].

In regard to the time of sonication, the longer the working time, the lower the size of the flakes. The typical area of the  $MoS_2$  flakes is around 25-250  $\mu m^2$ . We do not have to be worried about the time of the process since sonication is recognized as a nondestructive process, and we can rarely find defects on the basal plane of the flakes.

We prepare the catalyst by mixing 0.3 g of  $MoS_2$  with 60 ml of 2-Propanol (IPA) and exfoliating for 30 h using a sonotrode model CV 18 Sonics.

### 3.4.3 Centrifugation

The majority of the flake size resulting from exfoliation will be thick. We can separate thick flakes from thin flakes by means of centrifugation. Exposing the solution to ultra-centrifugation, we can separate particles with different sedimentation degrees thanks to centrifugal forces. The size of the flakes obtained is related to the speed of centrifugation: it has been demonstrated by analyzing many graphene samples with TEM technique that the dimensions of flakes obtained with a centrifugation at 3000 rpm are much smaller than flakes dimensions obtained with centrifugation at 500 rpm [34].

We centrifugate the catalyst for a time of 1h at 2000 rpm using a centrifuge 5424 Eppendorf.

### 3.4.4 Coating and mechanical interactions between catalyst and electrolyte

After exfoliation and centrifugation, the catalyst is ready to be coated on the GDL. We usually cut a rectangle of GDL from the carbon Fuelcellsetc paper with a surface of 10  $cm^2$ . By doing this, it makes it easier to choose the right load of the catalyst we will coat on the surface.

The first step is to measure the weight of the paper we have cut. In order to do that, we used a very accurate electronic balance by KERN ABS that can measure up to 10  $\mu g$ . After that, we put the carbon paper we have weighted in front of a 600 W lamp and we start to coat layer by layer the exfoliated  $MoS_2$  NFS onto the carbon paper by using a brush. The uniformity of the coating layer is very important because we want the entire surface to behave

in the same way. We have noticed that the highest the homogeneity, the better the performance of the battery.

After we pass one time with the brush, we have to wait until all the solvent (IPA) we used is completely dried by the heat of the light. We repeat this technique until we get the right load of catalyst. Then, we simply weigh the GDL again and take the difference between the new weight and the previous weight which resulted in the total weight of the load of the catalyst we coated on the GDL per  $cm^2$ .

At this step, it is useful to analyze and explain very briefly the reactions involved into the ORR on  $MoS_2$  NFs using pure  $EMIMBF_4$  saturated with 0.1 M of  $LiTFSI$  as electrolyte.

Figure 18 shows the reactions involved during the discharge process. We can notice that there are three main steps. In the first state it is shown that the cation  $EMIM^+$  strongly bonds to the negative  $Mo^-$  edge. It has been noticed that every edge of the catalyst is composed by  $Mo^-$  instead of  $S$  and the  $EMIM^+$  bonds with two atoms of  $Mo$ [33].

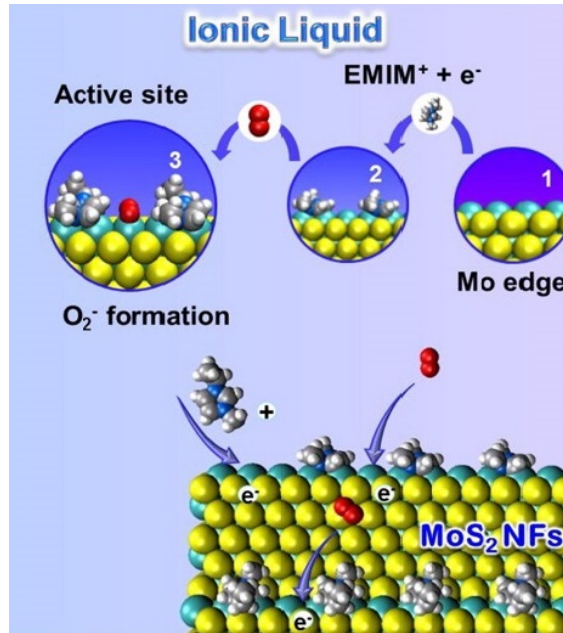


Figure 18: Mechanical interaction with the  $MoS_2$ , the Oxygen and the Ionic Liquid. Reprinted with permissions. Nature. [33]

In that way, the positive ion  $EMIM^+$  will cover the surface of the cathode during the discharge, avoiding that both the catalyst or the GDL degradate within the electrolyte. Since the coverage of the cathode surface is random and some  $EMIM^+$  atoms will be repelled if too close to each other, some Mo edges will not bond with the ionic liquid and they will be exposed to the solvent. Usually, the  $O_2$  needs two free electrons to complete dissociate. Since the Mo edge that have not been covered by the electrolyte are isolated, they will lead to the

formation of a  $O_2^-*$ . In this way, Oxygen does not dissociate, "leading to the formation of oxygen reduction sites" [33].

The isolated Mo edge are thus the active sites in which the reactions could happen. In this sites, the  $O_2^-$  reacts with the  $Li^+$  that comes from the dissolution of the anode within the electrolyte. Now, there are two possible scenarios of the reactions.

The first one is that the product  $Li_2O_2$  grows on the Mo free edge. This is not the case, because in that way the product will be stuck into the matrix pores, leading to bad electric performances of the battery.

The second one is that the anion  $O_2^-$  can desorb into the electrolyte and react with the  $Li^+$ , giving  $LiO_2$  as a product. Then,  $LiO_2$  will dissociate leading the formation of  $Li_2O_2$ , as we previously stated. This theory is consistent with the DEMS analysis that demonstrates the Lithium Oxide is the main product of the discharge.

Summarizing, we can state that the catalyst has two many important roles. The first one is to protect the cathode from the oxidation of its edges during the discharge. The second one is to let the Oxygen transform in  $O_2^-$  without completely dissociate. Therefore, the combination of  $EMIMBF_4$  and  $MoS_2$  leads to a synergistic effect between the two elements and, for that reason, to very high co-catalyst properties.

### **3.5    Design of the set-up**

Part of this work is to test how the impurities affect the electronic performances of the system. This step is very important since it is one of the last tests that have to be done in order to be able to put the battery on the market.

As matter of fact, in order to ensure a proper mode of working of the battery, a test with real conditions has to be done. In this case, it means the battery should work with real air, since oxygen is just a little percentage of the gases present in the atmosphere.

Because of that, the first step of this work has been to design a system that could be able to mimic real air conditions by controlling the gaseous percentages in it. We thought that a possible solution could be to design a system by which we could control the flow rate of different kind of gases and mix them all together, to obtain a final homogeneous well-known gas mixture. We built a hydraulic system made up of pipes, valves and mass flow controllers. We connected every gas cylinder to its own mass flow controller inlet in order to measure the volumetric flow rate and set it properly. We then connected every mass flow controller outlet to the mixer, a glass sphere with 4 inlets and 1 outlet. In this way, we can mix up to four different gases and get a homogeneous flow as an output.

In the next section, we will describe every component and we will analyze how the system works.

#### **3.5.1    Mass flow controllers**

The simplest solution is to adopt the mass flow controller technology since in this way we can ensure the best accuracy. The mass flow controller is a high technological device that can



both measure and control the flow rate of a gas through a closed-loop system. Even though the technology is so advanced, the way in which it works is quite simple. An inlet port, an outlet port, a sensor and a control valve compose the system. The gas gets into the mass flow controller through the inlet port and it flows into the main channel. Part of the fluid that flows in the channel is spilled out through a flow splitter, which is a narrow tube where inlet and outlet ports are located in the main channel (??). Since the diameter of the tube is so narrow, the fluid will be laminar. Due to this, results will be very accurate yielding in high repeat-ability since noises for a laminar fluid are negligible.

The thermodynamic sensor is the fundamental part of the whole system. It is composed by two resistors-thermometers that are wounded all around the bore pipe. When the current flows through the two resistors, the Ohms effect will heat up the tube. If there is no flow in it, the temperature profile will have a pyramidal shape, with the hottest side in the middle of the tube. The flow will also be heated up by passing through the two resistors. Consequently, the temperature shape will be shifted in the same direction of the flow motion, because of thermal exchange effects. Finally, the temperature measure is taken by calculating the difference of temperatures measured by the two thermometers and converted in electric input. We have to be aware that the sensors measure just a part of the flow; it means that the actual measure will be proportional to the real measure and it will be mathematically scaled to obtain the final and correct value.

The closed-loop system will automatically calculate the error between the theoretical value and the actual one and it will send as an output the current position of the control valve. In this way, we can guarantee a perfect constant flow rate at the outlet of the controller.

### 3.5.2 Mixer

In order to obtain a perfect homogeneous mixture, we now have to consider how the gases can be mixed together. We have to both consider the time needed to get a homogeneous mixture as well as the total dimension of the chamber. Moreover, we have to consider the pressure increment due to the presence of multiple gases in the same chamber.

The approach we adopted is the partial pressure law or Daltons law: every gas gives a single contribution to the total pressure of the system as if it occupies, alone, the entire volume of the chamber itself. The total pressure will be, finally, the sum that every gas pressure contributes.

$$p_{tot} = \sum p_{relative} \quad (3.2)$$

To design the mixer we made some important assumptions:

1. Theoretically, we can assume that there is no flow inside the mixer since the volume is quite big and flows are quite little. With this assumption, we can consider working in stationary conditions and we, definitely, simplify calculations because we can avoid the time dependence.
2. Ideal gases

3. Standard environment conditions, i.e.  $25^{\circ}\text{C}$  as atmospheric temperature and  $1\text{ atm}$  as atmospheric pressure
4. Maximum flow rate of  $100\text{ sccm}$
5. Maximum pressure we want to work with is  $1.05\text{ bar}$
6. Flow is real air with real percentages, i.e.  $72\%\text{ N}_2$ ,  $21\%\text{ O}_2$ ,  $0.05\%\text{ CO}_2$  and  $0.00001\%\text{ H}_2$  in volume

With those assumptions, we can calculate the number of moles of every gas in the chamber (working with a total mass flow rate of  $100\text{ [sccm]}$ ) and their own partial pressures. Lastly, using the ideal gas law and interpolating data we can find the best final volume of the chamber in order to get a maximum pressure of  $1.05\text{ [bar]}$ .

For safety reasons, we built the glass mixer with a thickness of  $3/8''$  in order to resist to a pressure of  $100\text{ [bar]}$ .

### **3.5.3 Pressure controllers and needle valves**

Since we mix more gases together, the density of the outlet flow will be different from the density of the inlet flow. That is the reason why the final volumetric flow rate of the mixture will be unknown and hard to calculate. We did not use a fifth mass flow controller since the final density of the flow rate will be very difficult to calculate with good accuracy. To avoid those problems, we decided to regulate the flow rate simply by using needle valves. In this way, we can easily regulate the flow by opening or closing the needles and measuring the pressure we get in the cell chamber with a vacuum pressure gauge to know how much fluid we are injecting in the cell chamber.

The needle valve is a high technology device that can regulate flow rates with a very high accuracy. Needle valves are always used in metering applications, especially with low flow rates. The orifice of this kind of valve is usually very narrow and the contact surface of the needle with the hole is so reduced that we could consider it as a line, not a surface. It means that the contact surface is very little and the flow would not leak in any way.

The vacuum pressure gauge is simply an item which can measure the relative pressure we have in a closed chamber.

Finally, with that configuration we can calculate exactly how much is the quantity of gas in the chamber of the cell and we can strongly know, with a quite good accuracy, what percentages of gas compose the mixture.

## CHAPTER 4

### RESULTS

#### 4.1 Previous results

Recent breakthroughs obtained by Amin Salehii-Khojin and Mohammad Asadi showed that a battery that works with pure  $O_2$  could have very high performances in terms of both efficiency and stability [33].

Cyclic voltammetry tests showed that the combination of Molibdenum Disulfite with the ionic liquid as electrolyte can lead to a very good performance of the cell in both ORR and OER with reduced polarization gap and with more than 80 % round-trip efficiency after 50 cycles.

Figure 19 shows the charge and discharge performances of the battery made of  $MoS_2$  as a catalyst with a load of  $0.2\text{ mg/cm}^2$  and  $EMIMBF_4$  ionic liquid as electrolyte saturated with 0.1 M of lithium salt  $LiTFSI$ . The battery has been tested with a capacity limit of 500  $mAh/gr$  with a current rate of 1000  $mA/gr$  up to 50 cycles. We have to clarify that from now on, both the current rate and the capacity are related to the mass of the  $MoS_2$  that has been coated on the cathode. The discharge at the first cycle reaches the desired capacity at 2.69 V. Instead, the charging process for 500  $mAh/gr$  is reached at 3.49 V: it means that the polarization gap obtained at this capacity is 0.8 V i.e. 85 % of efficiency. Moreover, results show that the cycle-ability is quite good because the polarization gap after 10 cycles is 0.85 V and

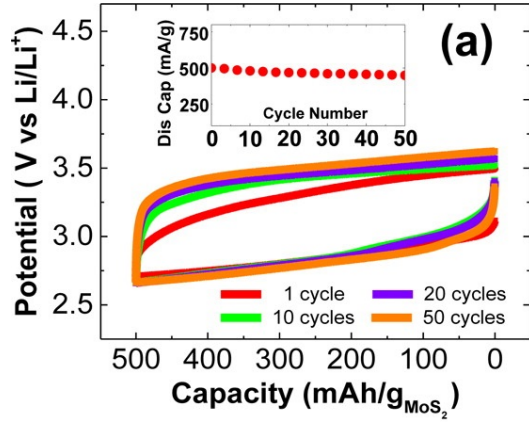


Figure 19: Charge and discharge battery performances with a 500  $\text{mAh/gr}$  limited capacity test at a current rate of 1000  $\text{mA/gr}$ . 50 cycles test [33]

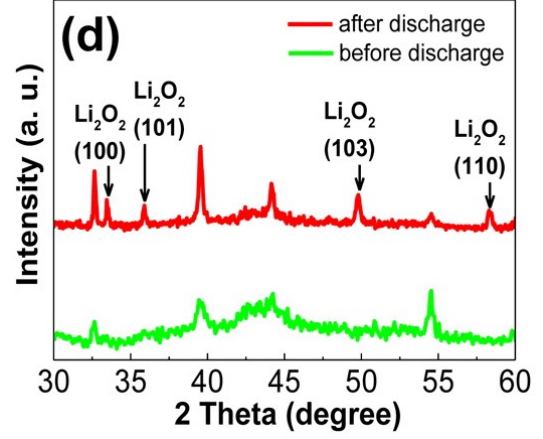


Figure 20: Cathode XRD analysis before and after discharge [33]

the long-term efficiency after 50 cycles was 80 %, which is better than most of the batteries we can find in the literature.

For the characterization of the cathode, SEM analysis have been performed before and after the discharge in order to analyze the surface area and the discharge Nano-particles. Moreover, X-Ray diffraction (XRD) and Raman spectroscopy analysis have been done in order to see the quality of the discharge products and it has been demonstrated that  $\text{Li}_2\text{O}_2$  was the main product either at the first cycle or at the 50th cycle (Figure 20).

Starting from this point, we will discuss all our experiments that we have done in order to improve the performances of the battery or to test it into a real environment.

#### 4.2 *MoS<sub>2</sub>* with pure IL saturated with 0.1 M *LiTFSI* as electrolyte with different mixtures of pure oxygen and carbon dioxide

The same cell has been tested in an atmosphere made of a mixture of  $O_2$  and  $CO_2$ . As we previously said,  $CO_2$  has an important impact on the performance of the cell since it takes part to the reactions. The catalyst is  $MoS_2$  with a load of  $0.2\text{ mg/cm}^2$  and the electrolyte is  $EMIMBF_4$  ionic liquid saturated with 0.1 M of lithium salt *LiTFSI*. Different percentages of  $CO_2$  in a pure  $O_2$  atmosphere have been tested.

Figure 21 shows the charge and discharge performances of the battery tested with a capacity limit of  $500\text{ mAh/gr}$  with a current rate of  $500\text{ mA/gr}$ . The percentages of  $CO_2$  that have been tested move from 0 % up to 100 %.

Working with pure  $O_2$ , the discharge at the first cycle begins at 2.9 V and the desired capacity is reached at 2.58 V. Instead, the charging process for  $500\text{ mAh/gr}$  is reached at 3.51 V: it means that the polarization gap we obtained at this capacity is 0.93 V.

With just 5 % of  $CO_2$  in the mixture, i.e. 50,000 ppm, the discharge at the first cycle begins at 3 V and the desired capacity is reached at 2.59 V: we can see that the discharge does not change dramatically. Instead, the charging process for  $500\text{ mAh/gr}$  is reached at 3.75 V: it means that the polarization gap we obtained at this capacity is 1.16 V. We have to consider that the quantity of  $CO_2$  tested is a way higher if compared to the  $CO_2$  present in real air, which is never more than 400 ppm.

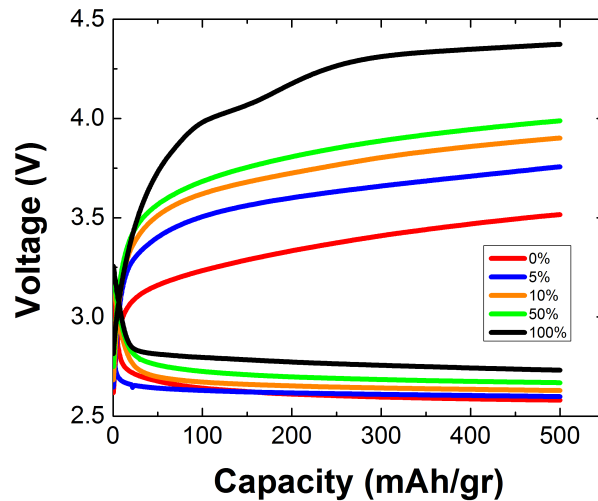


Figure 21: Charge and discharge battery performances with a 500  $\text{mAh/gr}$  limited capacity test at a current rate of 500  $\text{mA/gr}$  with different percentages of  $\text{CO}_2$  in pure  $\text{O}_2$

With pure  $\text{CO}_2$ , the discharge at the first cycle begins at 3.08 V and the desired capacity is reached at 2.73 V. Instead, the charging process for 500  $\text{mAh/gr}$  is reached at 4.37 V: it means that the polarization gap we obtained at this capacity is 1.64 V. We can notice that the performance of the cell at the first cycle dramatically decreases by increasing the quantity of the carbon dioxide in the mixture.

As we can notice, rather than the discharge, the main issue is the charge process. We can explain this fact saying that the voltage in charge increases by increasing the  $\text{CO}_2$  quantity because of thermodynamic reasons: since the product of the reaction  $\text{Li}_2\text{CO}_3$  has a higher



stability respect to  $Li_2O_2$ , the decomposition in  $Li^+$  and  $O_2$  will require a higher energy to be activated and this is translated into a higher voltage during the charge.

### **4.3 $MoS_2$ with different mixtures of IL in pure $DMSO$ saturated with 0.1 M $LiTFSI$ as electrolyte with pure oxygen**

At this point, we have demonstrated that the use of  $EMIMBF_4$  as electrolyte could be useful to obtain a battery that can show high performances both with pure  $O_2$  and with little amounts of  $CO_2$ . The second step of this work has been to try to make some changes on the electrolyte. The idea we developed has been to mix the ionic liquid with different concentrations into pure  $DMSO$ , seeing the effects on the charge and discharge electric performances were. Cyclic-voltammetry tests with different quantities of IL in  $DMSO$ , such as 10 % 25% or 50 %, have been done.

After having demonstrated that the the highest current in the Cyclic voltammetry test has been obtained with a mixture of 25% of IL in pure  $DMSO$  saturated with 0.1 M of  $LiTFSI$ , we tested the electrolyte in the real battery. The improvements compared to the pure IL are remarkable.

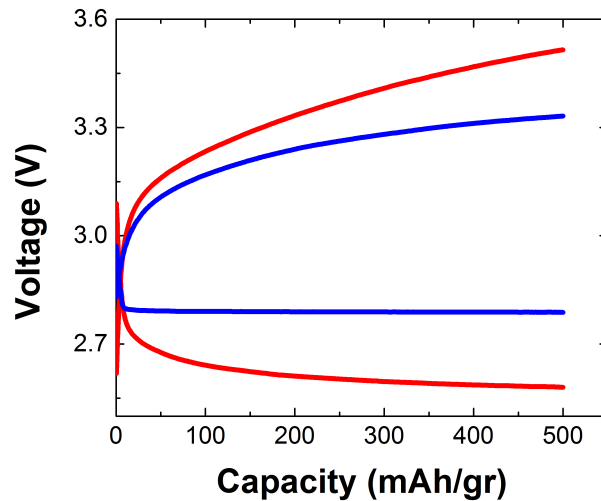


Figure 22: Charge and discharge battery performances with a 500  $mAh/gr$  limited capacity test at a current rate of 500  $mA/gr$  with pure Oxygen. Comparisons between the performance with pure IL saturated with *LiTFSI* 0.1 M and with 25 % of IL in pure *DMSO* saturated with *LiTFSI* 0.1 M as electrolytes

Figure 22 compares the charge and discharge performances of the pure IL battery and the mixed *IL-DMSO* battery for the first cycle, tested with a capacity limit of 500  $mAh/gr$  and with a current rate of 500  $mA/gr$ . The desired capacity in discharge is reached at 2.8 V, a way higher if we compare it to the previous 2.58 V we obtained with pure IL. The charging process for 500  $mAh/gr$  is reached at 3.31 V instead of 3.51 V: it means that the polarization gap we obtained at this capacity is 0.51 V, 40 % less of the polarization gap we obtained with pure IL.

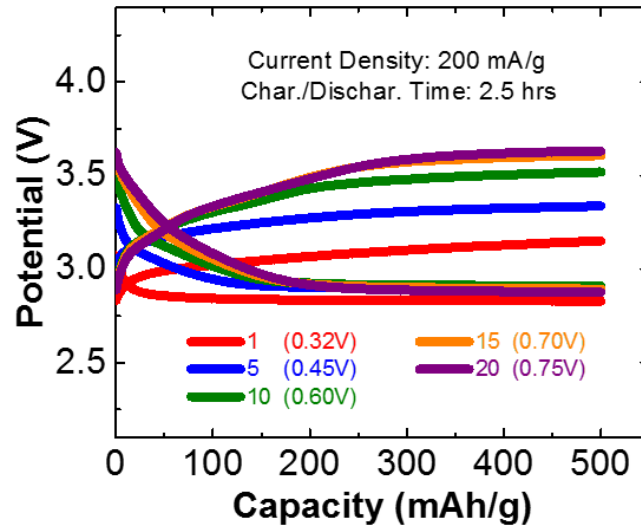


Figure 23: Charge and discharge battery performances with a 500  $mAh/gr$  limited capacity test at a current rate of 200  $mA/gr$  with 25 % of IL in pure *DMSO* saturated with 0.1 M of *LiTFSI* as electrolyte. 20 cycles test

The main positive effect is due to the combination of two different solvents that leads to an increase of the ionic conductivity: decreasing the potential reached at the complete charge, the polarization gap is noticeably reduced.

The issue that we noticed is that the cycle-life of the battery is reduced. Figure 23 shows the charge and discharge performances of the battery for a capacity limit of 500  $mAh/gr$  with a current rate of 200  $mA/gr$  for 20 cycles. The targeted capacity is reached during the discharge at 2.8 V and a complete discharge at 3.12 V, leading to a polarization gap of 0.32 V only. As we can notice, the polarization is quite reduced when we work with a lower current rate. As we

previously explained, the lower is the current, the best will be the performance of the battery. The problem is that the efficiency after the 20st cycle is a way reduced. As a matter of fact, at the 20st cycle, the targeted capacity is reached during the discharge at 2.8 V but the complete charge at 500  $mAh/gr$  is reached at 3.55 V, leading to a polarization gap of 0.75 V, more than twice of the first cycle. The phenomena is due to the high percentage of *DMSO*: even if it has been demonstrated that *DMSO* leads to a high reversibility of the discharge products, it is also true that the *DMSO* is not inert as ILs and for that reason it reacts with the sub-products of the reactions, which irreversibly leads to the passivation of the anode with a uncondutive SEI. This fact dramatically influences the electric properties of the cell during the time, leading to a worst cycle-ability.

#### **4.4 *MoS<sub>2</sub>* with 25 % of IL in pure *DMSO* saturated with 0.1 M of *LiTFSI* as electrolyte with pure oxygen and anodic passivation**

One of the biggest issues of the Lithium-air battery is its short cycle-life. Focusing the attention on the anode issue only, the problem is basically given by the growth of dendrites on the anode surface which electrically isolates the active lithium from the anode. Moreover, the formation of a uncondutive layer on the anode caused by the reaction between either solvent or impurities with the Lithium, which is very reactive, can cause many electrical problems such as high resistance and low reversibility of the reactions.

Recently, it has been demonstrated that carbon dioxide could enhance the performances of the battery, especially in its cycle-ability. As a matter of fact, it has been shown that the cycle-ability of a cell could be increased if the anode has been previously chemically treated

with  $CO_2$  [35]. The fact is that the Lithium reacts with both the  $CO_2$  and the electrolyte generating a thin layer on the anode surface. SEM analysis showed that the passivated anode present a very smooth surface without any dendrites on it after cycling the battery [35].

For that reason, in order to improve the cycle-ability of the battery, we passivated the anode by running the battery made of  $MoS_2$  with 25 % of IL in pure *DMSO* saturated with 0.1 M of *LiTFSI* for 5 cycle with a capacity-limited of 500 *mAh/gr* and a current rate of 500 *mA/gr* with pure  $CO_2$ .

After that process, we saved the anode and we assembled a new battery with the same elements but with the passivated anode.

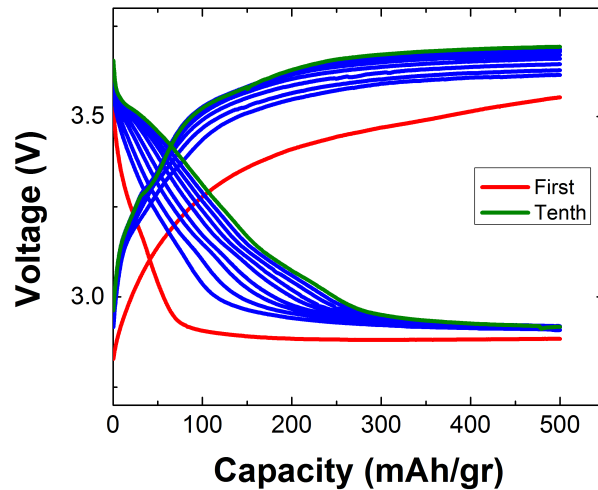


Figure 24: Charge and discharge battery performances with a 500  $mAh/gr$  limited capacity test at a current rate of 500  $mA/gr$  with 25 % IL in pure *DMSO* saturated with 0.1 M *LiTFSI* as electrolyte with pure  $O_2$ . 10 cycles test

Figure 24 shows the charge and discharge performances of the battery tested with a capacity limit of 500  $mAh/gr$  with a current rate of 500  $mA/gr$  up to 10 cycles.

The discharge at the first cycle reaches the desired capacity at 2.85 V. Instead, the charging process for 500  $mAh/gr$  is reached at 3.55 V: it means that the polarization gap we obtained at this capacity is 0.70 V. If we take a look to the tenth cycle, we can notice a quite stability of the battery. The complete discharge for a capacity of 500  $mAh/gr$  is obtained at 2.9 V. Instead, the complete charge at the labeled capacity is obtained at a voltage of 3.7 V, leading to a polarization gap of 0.8 V. If we compare the results with the performances of the same

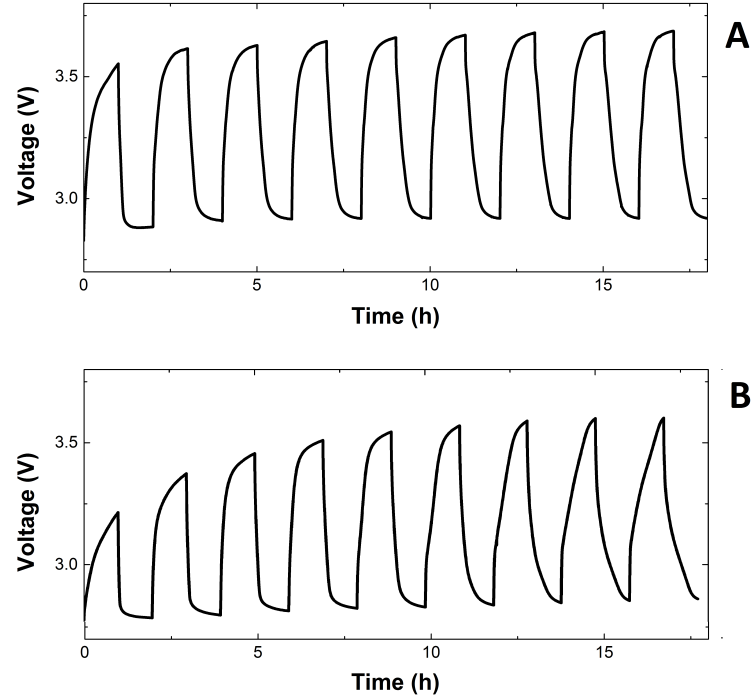


Figure 25: Charge and discharge battery performances with a  $500 \text{ mAh/gr}$  limited capacity test at a current rate of  $500 \text{ mA/gr}$ .

(A) Charging and discharging profiles of the first 10 cycles with anodic passivation. (B) Charging and discharging profiles of the first 10 cycles without anodic passivation

battery with a non treated anode, we can notice that the cycle-ability is improved, as expected.

Figure 25 (A) and Figure 25 (B) show the performance differences of the two different batteries: the first figure represents the performances in charge and discharge of the battery with the passivated anode, the second one shows the performances of the non passivated anode. We can notice in Figure 25 (B) that the first cycle is quite better respect to the first cycle of

Figure 24 (A). As a matter of fact, the labeled capacity of  $500 \text{ mAh/gr}$  is reached at 2.78 V. Instead, the charge is completed at 3.21 V, leading to a polarization gap of 0.43 V. The fact was expected since the passivated layer on the anode surface will increase the resistance, enhancing the voltage as an effect. But, we can notice that the gap at the tenth cycle increases a lot, up to 0.8 V.

In this way, the difference between the polarization gaps between the first and the tenth cycle with the protected anode is of 0.1 V only. Instead, for the battery without anodic protection, the difference is 0.37 V, three times more.

Therefore, it is shown that the anodic protection has a quite good effect and it can enhance the life of the battery. Moreover, improvements could be done on the passivating process: we think that is possible to get a thinner deposited surface in order to decrease the polarization gap at the first cycle, getting the same improvements on the cycle-ability.

#### **4.5 Improvement of the cycle-life adding $CO_2$ to pure $O_2$ with $MoS_2$ and 25 % of IL in pure $DMSO$ saturated with $LiTFSI$ 0.1 M as electrolyte**

The same concept we just mentioned could be applied in a different way. In this case, we tried to add a very little percentage of  $CO_2$  (less than 1 % in volume), in the gas mixture. In this way, a thin anode surface layer could be produced and the cycle-ability of the battery could thus be improved. Figure 26 shows the charge and discharge performances of the battery tested with a capacity limit of  $500 \text{ mAh/gr}$  with a current rate of  $200 \text{ mA/gr}$ . The battery is made of  $MoS_2$  as catalyst and 25 % of IL in pure  $DMSO$  saturated with 0.1 M  $LiTFSI$  as electrolyte. The desired capacity at the first cycle is reached at 2.79 V. Instead, the charging



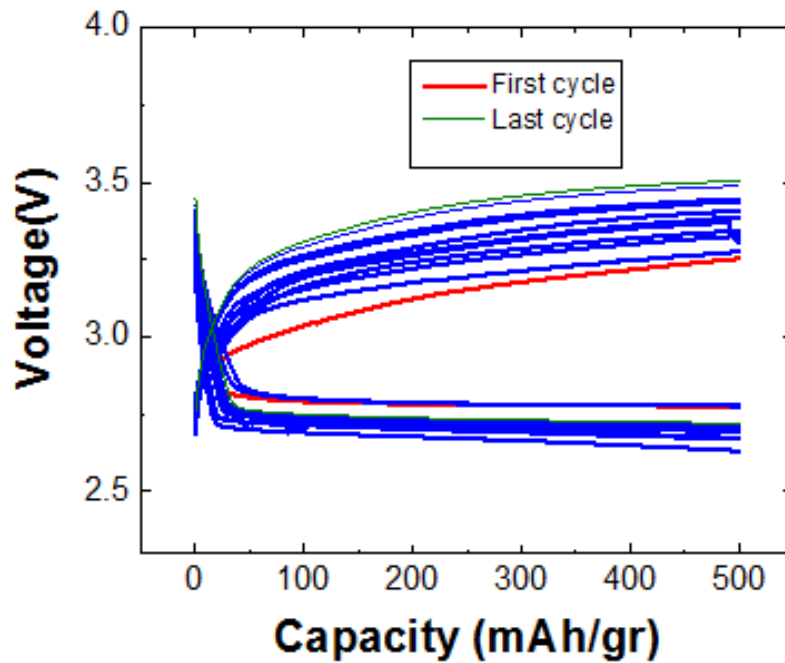


Figure 26: Charge and discharge battery performances with a  $500 \text{ mAh/gr}$  limited capacity test at a current rate of  $500 \text{ mA/gr}$  with 25 % of IL in pure *DMSO* as electrolyte with 1 % of  $\text{CO}_2$  in pure  $\text{O}_2$ . 10 cycles test

process for  $500 \text{ mAh/gr}$  is reached at 3.28 V: it means that the polarization gap we obtained at this capacity is 0.49 V.

Figure 23 showed that the initial polarization gap at the first cycle was 0.32 V. This is consistent with what we previously said since the energy required for the  $\text{Li}_2\text{CO}_3$  is higher than the energy required for the decomposition of  $\text{Li}_2\text{O}_2$ . The fact is demonstrated also by the

trends of the two different performances: while the discharge processes are quite similar, the charge process with the battery that works with 1 % of  $CO_2$  in the mixture increases faster respect to the other, reaching a higher voltage at the complete charge.

After 15 cycles, the desired capacity is reached at 2.72 V in discharge. Instead, the complete charge is reached at 3.5 V, leading to a polarization gap of 0.78 V. Comparing to Figure 23, the gap we obtained after 15 cycles was 0.7 V.

The difference between the polarization gaps for the first cycle and the 15th with 1 % of  $CO_2$  added is 0.3 V, instead it is 0.38 V with pure  $O_2$ .

This fact confirms that if we add a little percentage of  $CO_2$  into the mixture, even if the polarization gap is higher, we improve the cycle-ability.

#### 4.6 *MoS<sub>2</sub>* with 25 % of IL in *DMSO* saturated with 0.1 M of *LiTFSI* with different mixtures of pure oxygen and carbon dioxide

Since we noticed that the combination of *IL* and *DMSO* could be a good option, we decided to study what the effect of *CO<sub>2</sub>* was on the performances of the battery.

The catalyst is *MoS<sub>2</sub>* with a load of 0.1 *mg/cm<sup>2</sup>* and the electrolyte is made of 25 % of IL in pure *DMSO* saturated with 0.1 M of *LiTFSI*. Different percentages of *CO<sub>2</sub>* in a pure *O<sub>2</sub>* atmosphere have been tested.

Figure 27 shows the charge and discharge performances of the battery tested with a capacity limit of 500 *mAh/gr* with a current rate of 500 *mA/gr* . The percentages of *CO<sub>2</sub>* that have been tested move from 0 % up to 100 %.

Working with pure *O<sub>2</sub>* , the desired capacity in discharge is reached at 2.78 V. Instead, the charging process for 500 *mAh/gr* is reached at 3.33 V: it means that the polarization gap we obtained at this capacity is 0.55 V.

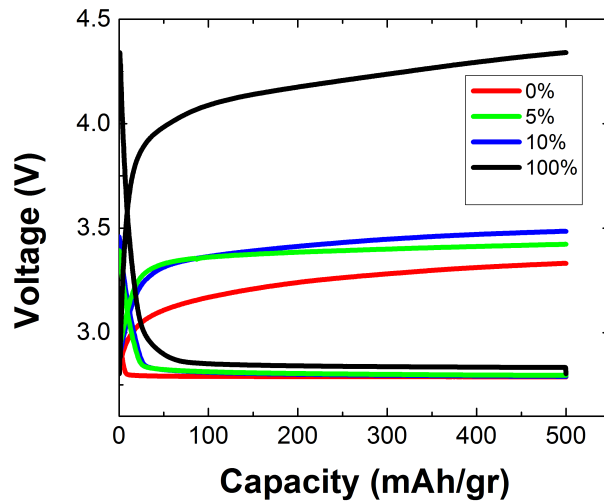


Figure 27: Charge and discharge battery performances with a 500  $mAh/gr$  limited capacity test at a current rate of 500  $mA/gr$  with 25 % of IL in pure *DMSO* saturated with *LiTFSI* 0.1 M as electrolyte with different percentages of  $CO_2$  in pure  $O_2$

With just 5 % of  $CO_2$  in the mixture, i.e. 50,000 ppm, the labeled capacity in discharge is reached at 2.78 V: we can see that the discharge does not change. Instead, the charging process for 500  $mAh/gr$  is reached at 3.42 V: it means that the polarization gap we obtained at this capacity is 0.64 V. Once again, we can notice that the battery reacts in a better way to the effect of  $CO_2$  respect to the battery that has pure ionic liquid as electrolyte.

The gap dramatically increased when we tried to work with pure  $CO_2$ . The total gap for the first cycle is 1.5 V. We have to clarify that for this experiment we use the same battery for both 10 % and 100 %. There is a possibility that some oxygen was still in chamber or that

some products of the previous charge and discharge processes reacted with  $CO_2$ . Anyway, we can still notice that the gap is decreased compared to the pure IL battery.

The fact that the charge is better could be related to the high solubility of  $CO_2$  in the *DMSO*. As a matter of fact, the  $CO_2$  solubility is fifty times higher compared to the solubility of the  $O_2$ : this fact could help the charge decreasing the energy required for the decomposition.

#### **4.7 $MoS_2$ with 25 % of IL in *DMSO* saturated with 0.1 M of *LiTFSI* as electrolyte with real air and with anodic passivation**

The crucial point of this thesis is to test the battery with real air conditions. Our main idea is to build a battery that can work with a constant flow that would be sucked from the external environment by means of a pump, leading to a fresh air chamber. We already tested the effects of the  $CO_2$  on the electrical performances and we noticed that the effects are remarkable. However, we do not have to be worried about that, since the percentage of the  $CO_2$  is so low that it will not influence the battery: on the contrary, we demonstrated that a little bit of  $CO_2$  could enhance the cycle-ability of the battery.

Since we know that most of the air is composed by Nitrogen (almost 79 %), we should test the influence of the Nitrogen onto the battery. We already know that the  $N_2$  does not have any effect on the battery performances since it does not participate to the reactions because its high stability. In the other side, we do not know how much oxygen is required to have a complete oxide-reduction reaction and we thought that maybe this fact could decrease the electrical performances either by increasing the polarization gap or by reducing the cycle-life of the battery.

Also, we have to notice that a very little percentage of  $CO_2$  and  $H_2$  is present in the natural air: this fact could affect the properties even more. We tested the battery with dry air, since the effects of moisture are still unknown and this would be the next step of this research.

The air we tested is composed by:

1. 78 % of  $N_2$
2. 21 % of  $O_2$
3.  $H_2O < 2$  ppm
4.  $THC < 0.1$  ppm
5.  $CO_2 < 0.5$  ppm
6.  $CO < 0.5$  ppm

The catalyst is  $MoS_2$  with a load of  $0.1 \text{ mg/cm}^2$  and the electrolyte is made of 25 % of IL in pure  $DMSO$  saturated with 0.1 M of  $LiTFSI$ . The anode has been passivated with a layer of  $Li_2CO_3$ : the anode has been previously exposed to eleven cycles of charge and discharge with a limited- capacity test of  $500 \text{ mAh/gr}$  at a current rate of  $500 \text{ mA/gr}$  with pure  $CO_2$ .

Figure 28 shows the charge and discharge performances of the battery tested with a capacity limit of  $500 \text{ mAh/gr}$  with a current rate of  $500 \text{ mA/gr}$ . The discharge at the first cycle reaches the desired capacity at 2.83 V. Instead, the charging process for a capacity of  $500 \text{ mAh/gr}$  is reached at 3.55 V: it means the polarization gap obtained at this capacity is 0.72 V. We can notice that the gap is increased if compared to the first cycle of a battery that works with pure  $O_2$  and without any anodic protection: we previously showed that the polarization gap

for this set-up was of 0.51 V. This fact was expected because we already said that the anodic protection increases the polarization gap because of the added SEI on the anode that increases the resistance of the system. Also, we have to take in account that we are working with a mixture in which the Oxygen is not predominant.

The cycle-ability of this system is quite good. After 50 cycles, the performances are very similar to the first one: the discharge reaches the labeled capacity at 2.76 V and the complete charge at 500 *mAh/gr* is reached at 3.59 V, leading to a polarization gap of 0.83. The difference between the first and the last cycle is of 0.1 V only, a very good result if compared to the results we found in the literature. At this time, we can notice that the main problem is the discharge: this is due to the SEI that originates on the anode surface and that grows up from cycle to cycle, increasing its thickness. In that way, it increases the resistance of the system and it blocks the flow of  $Li^+$  that come from the anode more and more, decreasing the potential during the discharge.

Anyway, this result confirms that to work with a high performances battery that works with real air is possible. The efficiency of the charge and discharge at the first and the fiftieth cycle is quite good and it is more than 80 % even if we are working with air instead of pure  $O_2$ . Of course, performances can be increased even more, and researches are still going on.

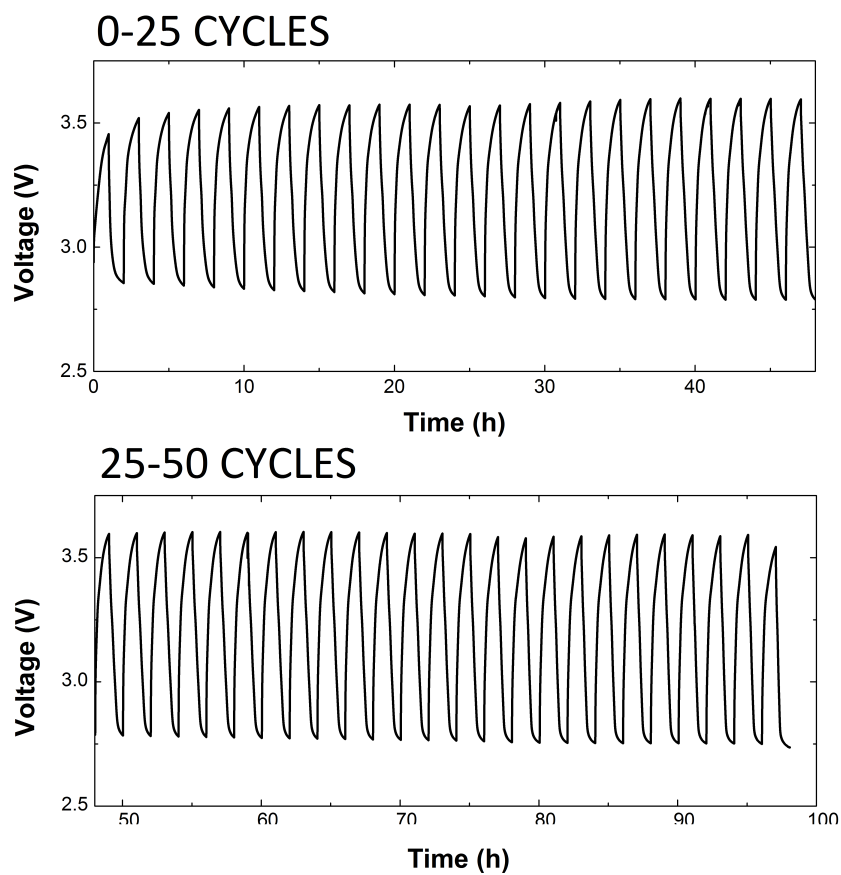


Figure 28: Charge and discharge battery performances with a  $500 \text{ mAh/gr}$  limited capacity test at a current rate of  $500 \text{ mA/gr}$  with 25 % of IL in *DMSO* saturated with 0.1 M *LiTFSI* as electrolyte with real air. 50 cycles test



## CHAPTER 5

### CONCLUSIONS

Even if Lithium-air batteries show very important electrical properties such as very high energy density, quite good efficiency and cycle-ability, they still need to be improved in order to be commercialized and inserted in the market.

In this research many findings have been done. First of all, a set up that is able to mimic real air conditions has been designed. The system is easily adaptable to many different conditions such as testing any kind of metal-gas battery with different gases or moisture.

Secondly, it has been found out that a mixture between organic (*DMSO*) and ionic liquid (*EMIMBF<sub>4</sub>*) could tune up the electrical performances of the battery. The best result that has been obtained is for a battery that works with a mixture of 25 % of IL in *DMSO* saturated with 0.1 M of *LiTFSI* as electrolyte with pure Oxygen. The polarization gap obtained in this way is, for a limited-capacity test of 500 *mAh/gr* at a current rate of 200 *mA/gr*, 0.32 V only. The polarization gap is incredibly lower if compared to the results we can find in the literature.

Also, the effect of the *CO<sub>2</sub>* on the battery charge and discharge performances has been analyzed and it has been demonstrated that *CO<sub>2</sub>* is an important parameter that has to be taken into account into the reactions. Surprisingly, it has been demonstrated that the battery can work into a proper way (or even better) when a little percentage of *CO<sub>2</sub>*, such as 1 % in volume, is present into the mixture.

An other important result is the positive effect of the anodic passivation. It has been demonstrated that the passivation of the anode with  $CO_2$  leads to positive effects such as the increase of the battery life.

Lastly, the battery has been tested with real air conditions. It has been found out that the high amount of Nitrogen does not affect the performances, such as the polarization gap or the stability of the battery during its life-time. The best result with real air, for a limited capacity test of  $500\text{ mAh/gr}$  at a current rate of  $500\text{ mA/gr}$ , shows a polarization gap of  $0.7\text{ V}$  at the first cycle and a polarization gap of  $0.83\text{ V}$  at the fiftieth cycle.

## APPENDIX

FIGURE 1: Carbon dioxide growth from 1958 until 2014 at Scripp's Mauna Loa Observatory.

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## APPENDIX (continued)

FIGURE 2: Carbon dioxide Emissions from Fuel Combustion (2012), International Energy Agency.

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Many thanks again and wishing you best of luck with your dissertation,

Eleonor

## APPENDIX (continued)

FIGURE 3: Specific energy densities of different Lithium-ions batteries relative to the electrodes materials (www.batteryuniversity.com)

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## APPENDIX (continued)

FIGURE 4: Theoretical and real energy densities of some kind of batteries compared to the gasoline energy density.

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**Title:** Lithium–Air Battery: Promise and Challenges

**Author:** G. Girishkumar, B. McCloskey, A. C. Luntz, et al

**Publication:** Journal of Physical Chemistry Letters

**Publisher:** American Chemical Society

**Date:** Jul 1, 2010

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## APPENDIX (continued)

FIGURE 5: Example of stability of a Lithium-air battery from cycle to cycle.

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## APPENDIX (continued)

FIGURE 6: Example of stability of a Lithium-ions battery from cycle to cycle.



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FIGURE 10: The main active materials specific energies and energy densities.

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FIGURE 12: Example of cycle-ability in a Lithium-air battery



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## APPENDIX (continued)

FIGURE 13: Viscosity of different ILs

FIGURE 14: Conductivity of different ILs

**Dr. Frank Stiemke**

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FIGURE 15: Chemical structure of the MoS<sub>2</sub>

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FIGURE 9: Scheme of the cell

FIGURE 16: Cyclic-Voltammetry test using MoS<sub>2</sub> as a catalyst with Oxygen and Argon

FIGURE 17: Current densities in the cathode led by different catalysts

FIGURE 18: Mechanical interaction with the MoS<sub>2</sub>, the Oxygen and the Ionic Liquid

FIGURE 19: Charge and discharge battery performances with a 500 mAh=gr limited capacity test at a current rate of 1000 mA=gr. 50 cycles test

FIGURE 20: Cathode XRD analysis before and after discharge



## CITED LITERATURE

1. Davis, S. J., Caldeira, K., and Matthews, H. D.: Future co<sub>2</sub> emissions and climate change from existing energy infrastructure. Science, 329(5997):1330–1333, 2010.
2. Quéré, C. L., Andres, R. J., Boden, T., Conway, T., Houghton, R., House, J. I., Marland, G., Peters, G. P., Van der Werf, G., Ahlström, A., et al.: The global carbon budget 1959–2011. Earth System Science Data, 5(1):165–185, 2013.
3. Cobb, J.: Top 6 plug-in vehicle adopting countries. HybridCars. com. Retrieved, pages 01–18, 2014.
4. Cars, H.: December 2012 dashboard. h ttp://www. hybridcars. com/december-2012-dashboard, accessed, pages 03–10, 2013.
5. Whittingham, M. S.: Electrical energy storage and intercalation chemistry. Science, 192(4244):1126–1127, 1976.
6. Wu, T. H., Pang, G. K., Choy, K., and Lam, H.: An optimization model for a battery swapping station in hong kong. In Transportation Electrification Conference and Expo (ITEC), 2015 IEEE, pages 1–6. IEEE, 2015.
7. Christensen, J., Albertus, P., Sanchez-Carrera, R. S., Lohmann, T., Kozinsky, B., Liedtke, R., Ahmed, J., and Kojic, A.: A critical review of li/air batteries. Journal of the Electrochemical Society, 159(2):R1–R30, 2011.
8. Girishkumar, G., McCloskey, B., Luntz, A., Swanson, S., and Wilcke, W.: Lithium-air battery: promise and challenges. The Journal of Physical Chemistry Letters, 1(14):2193–2203, 2010.
9. Kumar, B., Kumar, J., Leese, R., Fellner, J. P., Rodrigues, S. J., and Abraham, K.: A solid-state, rechargeable, long cycle life lithium–air battery. Journal of The Electrochemical Society, 157(1):A50–A54, 2010.
10. Bruce, P. G., Freunberger, S. A., Hardwick, L. J., and Tarascon, J.-M.: Li-o<sub>2</sub> and li-s batteries with high energy storage. Nature materials, 11(1):19–29, 2012.

## CITED LITERATURE (continued)

11. Deng, D.: Li-ion batteries: basics, progress, and challenges. Energy Science & Engineering, 3(5):385–418, 2015.
12. of Energy, U. S. D. and Jeppson, D.: Lithium literature review: lithium's properties and interactions. Department of Energy, 1978.
13. Rahman, M. A., Wang, X., and Wen, C.: A review of high energy density lithium–air battery technology. Journal of Applied Electrochemistry, 44(1):5–22, 2014.
14. Lu, J., Lee, Y. J., Luo, X., Lau, K. C., Asadi, M., Wang, H.-H., Brombosz, S., Wen, J., Zhai, D., Chen, Z., et al.: A lithium–oxygen battery based on lithium superoxide. Nature, 2016.
15. Zhang, T., Imanishi, N., Shimonishi, Y., Hirano, A., Xie, J., Takeda, Y., Yamamoto, O., and Sammes, N.: Stability of a water-stable lithium metal anode for a lithium–air battery with acetic acid–water solutions. Journal of the Electrochemical Society, 157(2):A214–A218, 2010.
16. Rahman, M. A., Wang, X., and Wen, C.: High energy density metal-air batteries: a review. Journal of The Electrochemical Society, 160(10):A1759–A1771, 2013.
17. Ottakam Thotiyil, M. M., Freunberger, S. A., Peng, Z., and Bruce, P. G.: The carbon electrode in nonaqueous li–o<sub>2</sub> cells. Journal of the American Chemical Society, 135(1):494–500, 2012.
18. Aurbach, D., Talyosef, Y., Markovsky, B., Markevich, E., Zinigrad, E., Asraf, L., Gnanaraj, J. S., and Kim, H.-J.: Design of electrolyte solutions for li and li-ion batteries: a review. Electrochimica Acta, 50(2):247–254, 2004.
19. Gittleson, F. S., Sekol, R. C., Doubek, G., Linardi, M., and Taylor, A. D.: Catalyst and electrolyte synergy in li–o<sub>2</sub> batteries. Physical Chemistry Chemical Physics, 16(7):3230–3237, 2014.
20. Lim, H.-K., Lim, H.-D., Park, K.-Y., Seo, D.-H., Gwon, H., Hong, J., Goddard III, W. A., Kim, H., and Kang, K.: Toward a lithium–air battery: The effect of co<sub>2</sub> on the chemistry of a lithium–oxygen cell. Journal of the American Chemical Society, 135(26):9733–9742, 2013.

## CITED LITERATURE (continued)

21. Faridbod, F., Rashedi, H., Ganjali, M. R., Norouzi, P., and Riahi, S.: Application of room temperature ionic liquids in electrochemical sensors and biosensors. INTECH Open Access Publisher, 2011.
22. Taberna, Y. G., Simon, P., and Energy, N.: Ionic liquids for electrochemical double layer capacitors a dissertation submitted to eth zurich for the degree of doctor of sciences presented by daniel...
23. Liu, X., Cui, B., Liu, S., and Chen, Y.: Progress of non-aqueous electrolyte for li-air batteries. Journal of Materials Science and Chemical Engineering, 3(05):1, 2015.
24. Yoshizawa, M., Hirao, M., Ito-Akita, K., and Ohno, H.: Ion conduction in zwitterionic-type molten salts and their polymers. Journal of Materials Chemistry, 11(4):1057–1062, 2001.
25. Trahan, M. J., Mukerjee, S., Plichta, E. J., Hendrickson, M. A., and Abraham, K.: Studies of li-air cells utilizing dimethyl sulfoxide-based electrolyte. Journal of The Electrochemical Society, 160(2):A259–A267, 2013.
26. Kwabi, D. G., Batcho, T. P., Amanchukwu, C. V., Ortiz-Vitoriano, N., Hammond, P., Thompson, C. V., and Shao-Horn, Y.: Chemical instability of dimethyl sulfoxide in lithium–air batteries. The journal of physical chemistry letters, 5(16):2850–2856, 2014.
27. Bieker, G., Winter, M., and Bieker, P.: Electrochemical in situ investigations of sei and dendrite formation on the lithium metal anode. Physical Chemistry Chemical Physics, 17(14):8670–8679, 2015.
28. Khan, A. and Zhao, C.: Oxygen reduction reactions in aprotic ionic liquids based mixed electrolytes for high performance of li–o<sub>2</sub> batteries. ACS Sustainable Chemistry & Engineering, 2015.
29. Meng, H. and Wang, C.-Y.: Electron transport in pefcs. Journal of the Electrochemical Society, 151(3):A358–A367, 2004.
30. Tran, C., Yang, X.-Q., and Qu, D.: Investigation of the gas-diffusion-electrode used as lithium/air cathode in non-aqueous electrolyte and the importance of carbon material porosity. Journal of Power Sources, 195(7):2057–2063, 2010.



### CITED LITERATURE (continued)

31. Kadantsev, E. S. and Hawrylak, P.: Electronic structure of a single mos 2 monolayer. Solid State Communications, 152(10):909–913, 2012.
32. Wang, Z. M.: MoS2: Materials, Physics, and Devices, volume 21. Springer Science & Business Media, 2013.
33. Asadi, M., Kumar, B., Liu, C., Phillips, P., Yasaei, P., Behranginia, A., Zapol, P., Klie, R. F., Curtiss, L. A., and Salehi-Khojin, A.: A cathode based on molybdenum disulfide nanoflakes for lithium–oxygen batteries. ACS nano, 2016.
34. Ciesielski, A. and Samorì, P.: Graphene via sonication assisted liquid-phase exfoliation. Chemical Society Reviews, 43(1):381–398, 2014.
35. Osaka, T., Momma, T., Matsumoto, Y., and Uchida, Y.: Surface characterization of electrodeposited lithium anode with enhanced cycleability obtained by co 2 addition. Journal of the Electrochemical Society, 144(5):1709–1713, 1997.
36. Asadi, M., Kumar, B., Behranginia, A., Rosen, B. A., Baskin, A., Repnin, N., Pisasale, D., Phillips, P., Zhu, W., Haasch, R., et al.: Robust carbon dioxide reduction on molybdenum disulphide edges. Nature communications, 5, 2014.
37. Aurbach, D., Gofer, Y., Ben-Zion, M., and Aped, P.: The behaviour of lithium electrodes in propylene and ethylene carbonate: Te major factors that influence li cycling efficiency. Journal of Electroanalytical Chemistry, 339(1-2):451–471, 1992.
38. Bi, Y., Wang, T., Liu, M., Du, R., Yang, W., Liu, Z., Peng, Z., Liu, Y., Wang, D., and Sun, X.: Stability of li 2 co 3 in cathode of lithium ion battery and its influence on electrochemical performance. RSC Advances, 6(23):19233–19237, 2016.
39. Chang, C. S., Low, J. S., and Srinivasan, D.: Application of tabu search in optimal system design and operation of mrt power supply systems. IEE Proceedings-Electric Power Applications, 146(1):75–80, January 1999.
40. Cindrella, L., Kannan, A., Lin, J., Saminathan, K., Ho, Y., Lin, C., and Wertz, J.: Gas diffusion layer for proton exchange membrane fuel cellsa review. Journal of Power Sources, 194(1):146–160, 2009.
41. Dahbi, M., Ghamouss, F., Tran-Van, F., Lemordant, D., and Anouti, M.: Comparative study of ec/dmc litfsi and lipf 6 electrolytes for electrochemical storage. Journal of Power Sources, 196(22):9743–9750, 2011.

## CITED LITERATURE (continued)

42. Deng, D.: Li-ion batteries: basics, progress, and challenges. Energy Science & Engineering, 3(5):385–418, 2015.
43. Dung, L.-R., Song, Z.-Y., and Yuan, H.-F.: An aging-compatible inductor-based equalization mechanism for lfp batteries. In Vehicle Power and Propulsion Conference (VPPC), 2015 IEEE, pages 1–6. IEEE, 2015.
44. Girishkumar, G., McCloskey, B., Luntz, A., Swanson, S., and Wilcke, W.: Lithium-air battery: promise and challenges. The Journal of Physical Chemistry Letters, 1(14):2193–2203, 2010.
45. Gowda, S., Brunet, A., Wallraff, G., and McCloskey, B.: Implications of co<sub>2</sub> contamination in rechargeable nonaqueous li–o<sub>2</sub> batteries. The journal of physical chemistry letters, 4(2):276–279, 2012.
46. Kafafi, Z., Hauge, R., Billups, W., and Margrave, J.: Carbon dioxide activation by lithium metal. 1. infrared spectra of lithium carbon dioxide (li+ co<sub>2</sub>-), lithium oxalate (li+ c<sub>2</sub>o<sub>4</sub>-), and lithium carbon dioxide (li<sub>2</sub>+ co<sub>2</sub>-) in inert-gas matrices. Journal of the American Chemical Society, 105(12):3886–3893, 1983.
47. Lim, H.-K., Lim, H.-D., Park, K.-Y., Seo, D.-H., Gwon, H., Hong, J., Goddard III, W. A., Kim, H., and Kang, K.: Toward a lithium–air battery: The effect of co<sub>2</sub> on the chemistry of a lithium–oxygen cell. Journal of the American Chemical Society, 135(26):9733–9742, 2013.
48. Nakai, K., Nakano, T., Hironaka, K., Higashimoto, K., Hara, K., Suzuki, K., and Iguchi, T.: Lithium-ion battery, September 10 2002. US Patent 6,447,946.
49. Olivier, J. G., Janssens-Maenhout, G., and Peters, J. A.: Trends in global co<sub>2</sub> emissions: 2012 report, 2012.
50. Takechi, K., Shiga, T., and Asaoka, T.: A li–o<sub>2</sub>/co<sub>2</sub> battery. Chemical Communications, 47(12):3463–3465, 2011.
51. Takechi, K., Shiga, T., and Asaoka, T.: A li–o<sub>2</sub>/co<sub>2</sub> battery. Chemical Communications, 47(12):3463–3465, 2011.
52. Zhang, Z., Zhang, Q., Chen, Y., Bao, J., Zhou, X., Xie, Z., Wei, J., and Zhou, Z.: The first introduction of graphene to rechargeable li–co<sub>2</sub> batteries. Angewandte Chemie International Edition, 54(22):6550–6553, 2015.

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