

**The Race for the Future of Energy Storage:  
Sodium–Oxygen Battery**

BY

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THESIS

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## TABLE OF CONTENTS

<u>CHAPTER</u>		<u>PAGE</u>
<b>1</b>	<b>INTRODUCTION . . . . .</b>	<b>1</b>
1.1	A Brief History of Electricity and Energy Storage . . . . .	1
1.1.1	Taming Electricity . . . . .	1
1.1.2	The Birth and Evolution of Energy Storage . . . . .	4
1.2	Batteries Principles of Operation . . . . .	8
1.2.1	Discharge & Charge . . . . .	8
1.2.2	Basic concepts . . . . .	10
1.2.3	Electrochemical Principles and the Complex Reality . . . . .	13
1.3	State of the Art . . . . .	16
<b>2</b>	<b>METAL - AIR BATTERIES . . . . .</b>	<b>18</b>
2.1	The Future of Energy Storage . . . . .	18
2.2	Outlook of the System . . . . .	24
2.2.1	General Details . . . . .	24
2.2.2	Main Challenges . . . . .	27
2.3	Chemistry & Energy of Developed Batteries . . . . .	29
2.3.1	How to choose between metals . . . . .	29
2.3.2	Overview on the present of Me – O <sub>2</sub> batteries . . . . .	32
<b>3</b>	<b>SODIUM - OXYGEN BATTERY . . . . .</b>	<b>38</b>
3.1	Introduction . . . . .	38
3.1.1	General Characteristics . . . . .	38
3.1.2	Why Sodium could be better than Lithium? . . . . .	39
3.2	Reported Studies . . . . .	41
3.2.1	Product Structure and Characteristics . . . . .	41
3.2.1.1	The Superoxide is Cubic! . . . . .	41
3.2.1.2	Superoxide or Peroxide? . . . . .	43
3.2.1.3	Intrinsic Conductivity of Discharge Products . . . . .	46
3.2.2	Instability and Side-Products . . . . .	47
3.2.3	Discharge and Charge Reaction Paths . . . . .	51
3.2.4	Current Dependency of Shape, Size, and Distribution . . . . .	54
<b>4</b>	<b>EXPERIMENTAL SET-UP . . . . .</b>	<b>57</b>
4.1	Anode . . . . .	57
4.2	Separator and Electrolyte . . . . .	59
4.3	Cathode and Catalyst . . . . .	61
4.3.1	The Catalytic Activity of MoS <sub>2</sub> and EMIM – BF <sub>4</sub> . . . . .	63

## TABLE OF CONTENTS (continued)

<u>CHAPTER</u>		<u>PAGE</u>
	4.4 Assembling . . . . .	65
	4.5 Experiments . . . . .	67
<b>5</b>	<b>RESULTS . . . . .</b>	<b>70</b>
	5.1 Looking for the Best Combination of Electrolyte and Salt . .	70
	5.2 Systematic Study on Current rate and Salt Concentration . .	81
	5.3 Anode Passivation . . . . .	94
<b>6</b>	<b>CONCLUSION AND FUTURE WORK . . . . .</b>	<b>99</b>
	<b>CITED LITERATURE . . . . .</b>	<b>101</b>
	<b>VITA . . . . .</b>	<b>109</b>

## LIST OF TABLES

<u>TABLE</u>		<u>PAGE</u>
I	COMPARISON OF PRINCIPAL PARAMETERS FOR A ME-AIR BATTERY'S ANODE. . . . .	30

## LIST OF FIGURES

<b>FIGURE</b>		<b>PAGE</b>
1	Discharge process of a generic battery. . . . .	8
2	Charge process of a generic battery. . . . .	9
3	Commercially available batteries advances through time. . . . .	16
4	Theoretical gravimetric energy densities of Metal-air systems. . . . .	19
5	Global electricity production in 2014 divided per source. (Data source: Renwables 2016 global status report) . . . . .	22
6	Annual growth rate of electricity production from renewable sources from 1990 to 2015 in OECD countries. (Data source: Renwables 2016 global status report) . . . . .	22
7	Schematic representation of the assembly of a Swagelok cell. . . . .	66
8	First shallow cycle of a Na – O <sub>2</sub> Swagelok cell with 0.5 M of Na–TFSI dissolved in EMIM – BF <sub>4</sub> as electrolyte. . . . .	72
9	Shallow cycling of a Na – O <sub>2</sub> cell with 0.5 M of Na–TFSI dissolved in EMIM – BF <sub>4</sub> and DMSO (in relation 1/3) as electrolyte. . . . .	73
10	Shallow cycling of a Na – O <sub>2</sub> cell with 0.5 M of Na–triflate dissolved in EMIM – BF <sub>4</sub> and DMSO (in relation 1/3) as electrolyte. . . . .	74
11	Shallow cycling of two Na – O <sub>2</sub> cells with EMIM – BF <sub>4</sub> and DMSO (in relation 1/9) as electrolyte, a) 0.5 M of NaClO <sub>4</sub> , b) 0.5 M of Na–triflate. . . . .	75
12	Shallow cycling of a Na – O <sub>2</sub> cell with 0.5 M of Na–triflate dissolved in EMIM – BF <sub>4</sub> and TEGDME (in relation 1/3) as electrolyte. . . . .	76
13	Shallow cycling of a Na – O <sub>2</sub> cell with 0.5 M of NaClO <sub>4</sub> dissolved in TEGDME as electrolyte. . . . .	77
14	Shallow cycling of a Na – O <sub>2</sub> cell with 0.5 M of NaClO <sub>4</sub> dissolved in 75 % of TEGDME and 25 % of IL as electrolyte. . . . .	78
15	Shallow cycling of two Na – O <sub>2</sub> cells with 0.5 M of NaClO <sub>4</sub> dissolved in EMIM – BF <sub>4</sub> and TEGDME as electrolyte, a) 50 % of TEGDME and 50 % of IL, b) 90 % of TEGDME and 10 % of IL. . . . .	79
16	Shallow cycling of a Na – O <sub>2</sub> cell with 0.5 M of Na–triflate dissolved in 90 % of TEGDME and 10 % of IL as electrolyte. . . . .	81
17	Shallow cycling of a Na – O <sub>2</sub> cell with 0.5 M of NaClO <sub>4</sub> dissolved in 90 % of TEGDME and 10 % of IL as electrolyte at 0.1 mA/cm <sup>2</sup> . . . . .	82
18	Shallow cycling of a Na – O <sub>2</sub> cell with 0.5 M of NaClO <sub>4</sub> dissolved in 90 % of TEGDME and 10 % of IL as electrolyte at 0.2 mA/cm <sup>2</sup> . . . . .	84
19	SEM pictures at low magnification of the MoS <sub>2</sub> coated surface of the GDL (i.e. the cathode), a) Mag = 84 X, b) Mag = 1.27 K X. . . . .	85
20	SEM pictures at high magnification of the MoS <sub>2</sub> coated surface of the GDL (i.e. the cathode), a) Mag = 8.53 K X, b) Mag = 5.34 K X. . . . .	86

## LIST OF FIGURES (continued)

<u>FIGURE</u>		<u>PAGE</u>
21	Shallow cycling of a Na – O <sub>2</sub> cell with 0.5 M of NaClO <sub>4</sub> dissolved in 90 % of TEGDME and 10 % of IL as electrolyte at 0.3 mA/cm <sup>2</sup> . . .	88
22	Shallow cycling of a Na – O <sub>2</sub> cell with 0.5 M of NaClO <sub>4</sub> dissolved in 90 % of TEGDME and 10 % of IL as electrolyte at 0.025 mA/cm <sup>2</sup> . . .	89
23	Shallow cycling of a Na – O <sub>2</sub> cell with 0.5 M of NaClO <sub>4</sub> dissolved in 90 % of TEGDME and 10 % of IL as electrolyte at 0.2 mA/cm <sup>2</sup> . . .	91
24	Shallow cycling of two Na – O <sub>2</sub> cells with EMIM – BF <sub>4</sub> and DMSO (in relation 1/9) as electrolyte at 0.1 mA/cm <sup>2</sup> , a) 1 M of NaClO <sub>4</sub> , b) 2 M of NaClO <sub>4</sub> . . . . .	92
25	Shallow cycling of a Na – O <sub>2</sub> cell with 0.1 M of NaClO <sub>4</sub> dissolved in 90 % of TEGDME and 10 % of IL as electrolyte at 0.1 mA/cm <sup>2</sup> . . .	93
26	Shallow cycling of a Na – CO <sub>2</sub> cell with 0.5 M of Na–TFSI dissolved in 75 % of DMSO and 25 % of IL as electrolyte at 0.05 mA/cm <sup>2</sup> . . .	96
27	Shallow cycling of a Na – O <sub>2</sub> cell with 0.5 M of NaClO <sub>4</sub> dissolved in 90 % of TEGDME and 10 % of IL as electrolyte at 0.05 mA/cm <sup>2</sup> , after anode passivation. . . . .	97

## LIST OF ABBREVIATIONS

EMF	Electromotive Force
DC	Direct Current
AC	Alternate Current
Me	Metal
EV	Electric Vehicle
GM	General Motors
CEO	Chief Executive Officer
PHEV	Plug-in Hybrid Vehicle
BEV	Battery Electric Vehicle
OECD	Organisation for Economic Co-operation and Development
SEI	Solid Electrolyte Interface
TEM	Transmission Electron Microscopy
SEM	Scanning Electron Microscopy
ORR	Oxygen Reduction Reaction
OER	Oxygen Evolution Reaction

## LIST OF ABBREVIATIONS (continued)

PPTC	Proton Phase Transfer Catalyst
XRD	X-Ray Diffraction
DME	Dimethoxyethane
DGME	Diethylene Glycol Monoethyl Ether
DEGDME	Diethylene Glycol Dimethyl Ether
TEGDME	Tetraethylene Glycol Dimethyl Ether
DMSO	Dimethyl Sulfoxide
IL	Ionic Liquid
GDL	Gas Diffusion Layer
IPA	Isopropyl Alcohol
DMC	Dimethyl Carbonate

## SUMMARY

Battery evolution is targeting always smaller, lighter, and less expensive systems in order to keep up with electronics development. Electric vehicles are starting to spread in many countries and several multinational car corporations, captained by Tesla, are investing in this technology. Moreover it is just a matter of time before also the electric grid would need powerful batteries to implement the renewable energies, overcoming the issue of discontinuous production.

The two main limitations of today Li-ion batteries are the energy density and the high cost. Remarkable improvements are needed to meet future requirements and it is progressively clearer that we are reaching the maximum exploitation of that system.

The question is which revolutionary battery will replace Li-ion and become the pivot of the energy storage of tomorrow?

Metal-air batteries are considered from lots of scholars as the system of the future. They have an astonishing energy density, one order of magnitude higher than the ones of Me-ion and they are less expensive. Among those new type of batteries the most studied has been Li-air, yet some complications delayed the obtaining of a practical battery and some researchers started to look around to find other possible metals to employ as anode.

Sodium turned out to be one of the most promising candidates, thanks to its abundance on the Earth crust (2.83% vs. 0.0018% of Lithium), its low cost (1.7 \$/kg vs. 68 \$/kg of Lithium), and its high efficiency, due to one-electron transfer reactions.

## SUMMARY (continued)

This thesis reports the experimental work done at the Nanomaterials Energy Systems Laboratory at UIC, finalized to the study of Sodium–Oxygen battery. From the preparation of anode and MoS<sub>2</sub> nanoflakes coated carbon cathode, to the discharge–charge cycling of the cells. First we explored different electrolytes and salts, to find the best combination. Then we performed a systematic study on the influence of current rates and salt concentrations on the performance, and finally we began to analyze the passivation of the anode to protect it against side–reactions and poisoning.

## CHAPTER 1

### INTRODUCTION

#### 1.1 A Brief History of Electricity and Energy Storage

##### 1.1.1 Taming Electricity

The discovery of static electricity is one of the oldest made by human beings, but it remains unexplained and a merely interesting phenomenon for centuries. The first reported study regarding electricity was probably the one conducted by the Greek philosopher Thales of Miletus (c. 624 – 546 B.C.), who observed that amber (in ancient Greek: *electron*), if rubbed, attracts light objects, like hair for example. Centuries passed without any relevant progress, since the beginning of Renaissance, when scholars from different countries started to explore more in deep the laws behind electricity. Despite the increased scientific attraction of this subject, we have to wait till the 18<sup>th</sup> century to finally see a real theory about electricity.

Benjamin Franklin and Giambatista Beccaria through a process of observations and hypothesis, independently formulated a description of electricity as a fluid, made of microscopic particles, which could have a kind of positive or negative energy.

They widened the door of the modern electrostatics, Charles Augustin de Coulomb between 1785 and 1791 published his famous studies about the attraction and repulsion laws of electric particles (Equation 1.1 and Equation 1.2).

$$F = k \cdot \frac{|q_1| \cdot |q_2|}{d^2} \quad (1.1)$$

Where:

**F** is the Coulomb force between two electric particles;

$q_1$  **and**  $q_2$  are two point charges;

**d** is the distance between the particles;

**k** is the Coulomb constant  $k = 1/4\pi\epsilon_0 = 8.9 \cdot 10^9 \text{ Nm}^2\text{C}^{-2}$ .

$$E = \frac{F}{q_0} \quad (1.2)$$

Where:

**E** is the electrostatic field;

$q_0$  is the electric charge which produce the field, that is independent from the test charge.

Subsequently, in the 1826 André-Marie Ampère explained the relation between electricity and magnetism coming up with the formulation of the so called "Ampère's law" (Equation 1.3), marking the beginning of the electromagnetism.

$$\oint_C B dl = \mu_0 \iint_S J dS = \mu_0 \cdot \quad (1.3)$$

Where:

$\mathbf{B}$  is the magnetic field;

$\mu_0$  is the permeability of vacuum or magnetic constant;

$\mathbf{J}$  is the current density;

$I_{enc}$  is the total current passing through a surface S enclosed by C.

During the same year George Simon Ohm published the three "Ohm's laws" (Equation 1.4, Equation 1.5 and Equation 1.6) about the electric resistance.

$$R = V/I \tag{1.4}$$

$$R = \rho \, l/S \tag{1.5}$$

$$P = V \cdot I = R \cdot I^2 \tag{1.6}$$

Where:

$\mathbf{R}$  is the electric resistance;

$\mathbf{V}$  is the voltage;

$\mathbf{I}$  is the current;

$\rho$  is the resistivity;

$\mathbf{l}$  is the conductor length;

$\mathbf{S}$  is the conductor section.

Few years later, in the 1831, Micheal Faraday discovered the "Faraday's law of induction" (Equation 1.7), predicting how the interaction between a magnetic field and an electric circuit could produce an electromotive force (EMF).

$$\varepsilon = -\frac{d\Phi_B}{dt} \quad (1.7)$$

Where:  $\varepsilon$  is the electromotive force and  $\Phi_B$  is the magnetic flux.

Finally, between 1861 and 1862 James Clerk Maxwell published the famous "Maxwell's equations", four partial differential equations that enclose the foundation of classical electromagnetism.

The theorization of electricity and magnetism led a technological revolution which started with electricity and light distribution, thanks to Tesla and the alternate current, and in the subsequent decades continued with electric motors and wireless communication through radio-waves and then the invention of phones, cameras, televisions, computers and all the electric devices we use nowadays.

### **1.1.2 The Birth and Evolution of Energy Storage**

When in the 1799 Alessandro Volta, continuing the studies made by Luigi Galvani on the electric current, succeeded in the realization of the first electrochemical battery ever, he did not understand exactly the real mechanisms behind the functioning of his invention and he surely

could not even imagine that it would become a fundamental component of all the electronics devices of the future.

An electric battery is a device which converts chemical energy, hidden in chemical bonds between molecules, in electric energy available for a load. Nowadays the main and most useful benefit of using a battery is giving freedom from utility power. With batteries we could finally make electronic devices which are portable and have their own autonomy, we are no more confined by wires and sockets. However, at that time, the voltaic pile was even more, it was the first device capable of producing electrical energy. It was a discovery which would start a revolution in technology some decades later that would completely change the face of the world, but Volta could not realize this.

The voltaic pile consists in an alternate serie of copper and zinc plates, separated by paper disks imbued in a solution of water and sulfuric acid, everything maintained in a vertical position by the outer wooden structure. Connecting two copper wires respectively to the first and last plate, steady current could be produced for a considerable length of time.

Volta believed that the corrosion of the metals was a side-effect, due to the transit of current, rather than an unavoidable consequence of the operation principle of his device.

In the 1834 Michael Faraday, after deeply studying the phenomenon, realized that chemical reactions and ions movements were the foundation of the working of a battery. Two years later, in the 1836, John Frederic Daniell elaborated the investigation of Faraday and the brainchild of Volta and prototyped a new battery with enhanced performances and higher safety, what will be called the "Daniell cell".

The first practical source of electrical energy was born. It was a power source for industrial applications, which at the time was limited to electric telegraphs. Still it remained the only way to have electricity till the 1869, with the invention of the dynamo, the first electrical generator, which was rapidly followed by a number of other DC current generators and few decades later by the AC current generators. Those devices got easily ahead of batteries as far as concerns electrical energy production and pushed the transition of batteries to the field of energy storage.

The voltaic pile and the Daniell cell were what we now call *primary batteries*. These kind of batteries are not suitable for energy storage applications, since they are not capable of being recharged. Their reactions are practically irreversible, in fact they are disposable devices.

After Daniell, many other scholars designed different batteries, with various combinations of metals and several structures, still all grounded on the same physical and chemical principles. In fact, one century ahead, a complete set of primary batteries was on the market: Zinc, Alkaline, Mercury, Silver-oxide, Magnesium and Lithium.

Until the second half of the XX century primary batteries spread all over the world, becoming the unique source of electrical energy of quite all the portable devices. One problem was about to emerge, electronics was starting to grow faster and faster, requiring always more batteries and farther with more power and longer life.

Suddenly all the limitations of disposable devices started to become evident, the cost/duration ratio began to increase and problems on the waste disposal emerged, since almost all the batteries contained toxic agents.

Fortunately for us the solution was behind the corner, a new class of batteries were designed,

devices with a new skill, the energy storage.

*Secondary cells, accumulators, storage batteries*, finally batteries which can be recharged to their original condition and used many and many times. Sequentially, a set of secondary cells joined the market: Nickel–Cadmium, Lead–acid, Nickel–Zinc, Silver–Zinc and Lithium–ion (just to cite the main ones).

The research on rechargeable batteries led to the birth of many different devices and the infinite competition for the best performances is still going on. Recent developments drove Lithium-ion system to conduct the race. In fact nowadays the majority of electronics devices are powered by Lithium–ion batteries, from the small coin–cell inside your watch to the battery–pack of the Tesla Model S.

Despite the incredible progress of last years on Lithium–ion performances, we are well apart from reaching an equilibrium with electronics. The always increasing demand for portable energy requires continuum development on the energy storage side.

Experts are pretty sure that it will be difficult to further improve Li–ion system, which is reaching the limitations imposed by the materials themselves. That is why a new kind of batteries with a huge potential started to attract professors and research laboratories across the world: metal–air batteries.

## 1.2 Batteries Principles of Operation

### 1.2.1 Discharge & Charge

The operation of a rechargeable battery is made by two fundamental parts: discharge and charge.

During discharge the cell is connected to an external load, which implies a flow of electrons from the anode to the cathode (Figure 1). [1] The anode oxidizes, releasing electrons and positive ions (i.e. cations), while the cathode reduces, accepting electrons and forming negative ions (i.e. anions). The electric circuit is completed through the electrolyte, through which anions flow toward the anode and cations toward the cathode.

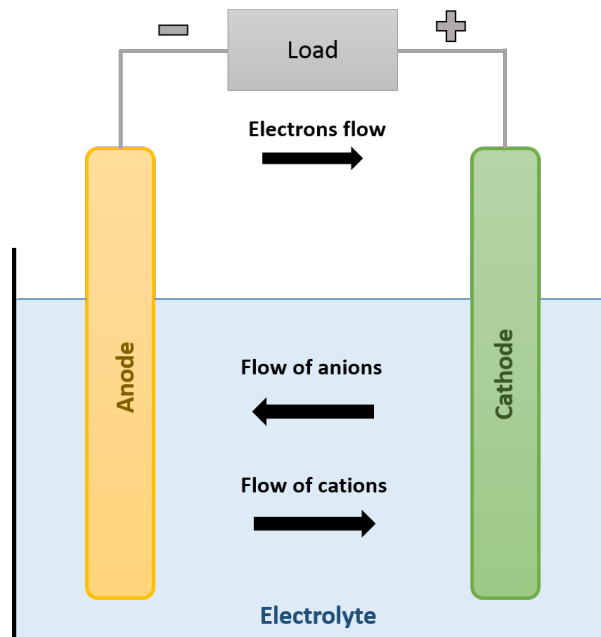
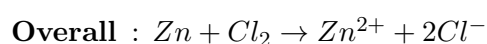
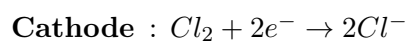
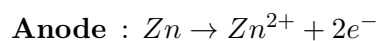


Figure 1: Discharge process of a generic battery.

Let's suppose to have a cell in which the anode is made of zinc (Zn) and the cathode is chlorine (Cl<sub>2</sub>). The reactions during the discharge would look as follows:



In order to recharge a secondary cell the current flow need to be reversed. During charge the negative electrode reduces, accepting electrons and reforming molecules, while the positive electrode oxidizes, reassembling molecules and releasing electrons. Since, by definition, the anode is the electrode where oxidation takes place, while the cathode is the one at which reduction occurs, it follows that during charge anode and cathode are reversed (Figure 2).

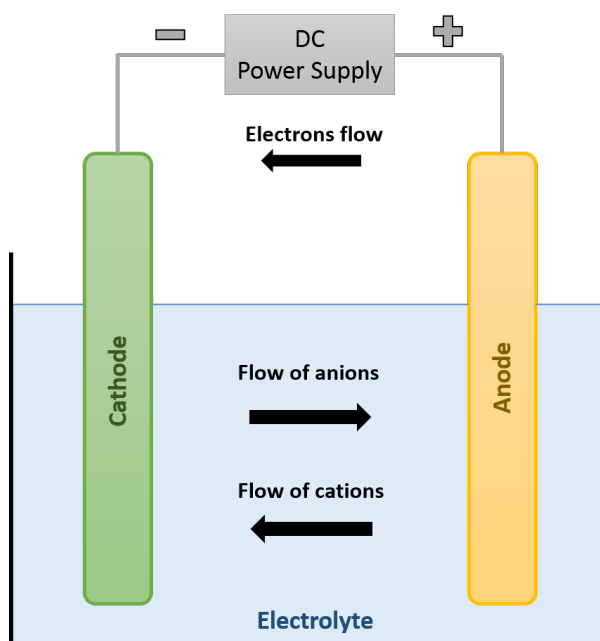
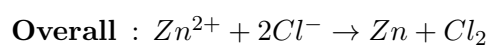
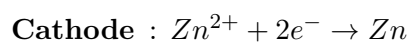
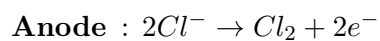


Figure 2: Charge process of a generic battery.

Continuing to analyze the previous cell, the reactions could be written as:



### 1.2.2 Basic concepts

According to the second law of thermodynamics (Equation 1.8), a reaction is defined spontaneous if it tends to increase the entropy (S) of the system.

$$\frac{dS}{dt} \geq 0 \quad (1.8)$$

The equilibrium of a thermodynamic system with constant pressure and temperature is regulated by the Equation 1.9.

$$\Delta G = \Delta H - T\Delta S \quad (1.9)$$

Where:

$\Delta G$  is the variation in Gibbs' free energy [J];

$\Delta H$  is the variation in enthalpy [J];

**T** is the absolute temperature [K];

$\Delta S$  is the variation in entropy [J/K].

If the Gibbs' free energy is negative the process is spontaneous.

In electrochemistry, at standard conditions, the Gibbs' free energy variation is regulated by the following relation (Equation 1.10).

$$\Delta G^0 = -nF\Delta E^0 \quad (1.10)$$

Where:

$n$  is the number of moles of electrons involved in stoichiometric reaction [mol];

$F$  is the Faraday's constant,  $F = 96.485 \text{ C/mol}$ ;

$\Delta E^0$  is the standard reduction potential [V].

Therefore "whenever a [natural] reaction occurs, a decrease in the free energy of the system" is experienced. [1]

If we need to explore the region outside the standard state, the voltage could be computed utilizing the so called "Nerst equation" (Equation 1.11).

$$E = E_0 - \frac{R}{n} \frac{T}{F} \ln \frac{a_C a_D}{a_A a_B} \quad (1.11)$$

Where:

$a_i$  are the values of activity of the different species;

$R$  is the gas constant ( $R = 8.314 \text{ J/mol K}$ );

$T$  is the absolute temperature [K].

The standard reduction potential is a feature of every material and is the potential referred to the standard hydrogen potential, arbitrarily defined null ( $E_{H_2}^0 = 0.00\text{V}$ ). It follows that we can determine the "*standard potential*" of a cell from the standard electrode potentials" (Equation 1.12). [1]

$$Anode_{oxidation\ potential} + Cathode_{reduction\ potential} = standard\ cell\ potential \quad (1.12)$$

For instance, let's consider again the previous cell made by zinc and chlorine and remember that the oxidation potential is the negative of the reduction one. At the anode side zinc oxidizes ( $Zn \rightarrow Zn^{2+} + 2e^-$ ), so the potential is  $-(-0.76\text{ V})$ , while at the cathode side chlorine reduces ( $Cl_2 + 2e^- \rightarrow 2Cl^-$ ) with a reduction potential of  $1.36\text{ V}$ , thus, summing those values we obtain the standard cell potential  $E^0 = 2.12\text{ V}$ .

Obviously things are not that simple and many other factors play an important rule in the evaluation of the cell voltage, as we will see in the next paragraph (1.2.3).

Another important parameter for a cell is the *theoretical energy*, also called *capacity*. This represents the maximum quantity of energy which an electrochemical system could deliver and is defined as follows (Equation 4.2).

$$Capacity\ [\text{Wh}] = Voltage\ [\text{V}] \cdot Current\ [\text{A}] \cdot Time\ [\text{h}] \quad (1.13)$$

It is worth saying that in practice just a fraction of the theoretical energy is produced by the system, since the cell is made by a few components (for example current collectors, separators, electrolyte, additives), each of them importing his own resistance and obstacles which distinguish theory from practice.[1]

### 1.2.3 Electrochemical Principles and the Complex Reality

When we start to move toward real electrochemical systems, processes become more tricky and we need to consider a wider range of factors.

First of all, when a current passes through the cell *polarization losses* arise:

- "Activation polarization, which drives the electrochemical reaction at the electrode surface;" [1]
- "Concentration polarization, which arises from concentration differences of the reactants and product at the electrode surface and in the bulk as a result of mass transfer." [1]

These phenomena consume a fraction of the theoretical energy, releasing it as waste heat. It is intricate, in practice, to take into account these effects, since the vast majority of batteries are complex systems made by highly porous cathodes, performance enhancing additives, one or more electrolytes, binders and catalysts. Hence a significant effort is needed to design mathematical models to estimate these losses more precisely.

The second factor that requires attention is the *internal impedance* of the cell, which produces a voltage drop typically called "ohmic polarization" or "IR drop" (proportional to the current rate flowing in the system). "The total internal impedance of a cell is the sum of the ionic resistance of the electrolyte (within the separator and the porous electrodes), the electronic resistances of the active mass, the current collectors and electrical tabs of both electrodes, and the contact resistance between the active mass and the current collector. These resistances are ohmic in nature, and follow Ohms law, with a linear relationship between current and voltage drop." [1]

The cell voltage ( $E$ ) could be calculated as:

$$E = E_0 - [(\eta_{a-p})_a + (\eta_{a-p})_c] - [(\eta_{c-p})_a + (\eta_{c-p})_c] - i \cdot R_i = i \cdot R \quad (1.14)$$

Where:

$E_0$  is the open circuit voltage;

$(\eta_{a-p})_a$ ,  $(\eta_{a-p})_c$  are the activation polarization increases of voltage at anode and cathode;

$(\eta_{c-p})_a$ ,  $(\eta_{c-p})_c$  are the concentration polarization increases of voltage at anode and cathode;

$i$  is the current rate;

$R_i$  is the total internal resistance;

$R$  is the external load.

Therefore we could easily deduce that a decrease in the current rate results in turn in a lower polarization effect and a smaller IR drop, which means that the cell is working closer to the

theoretical performance.

The last topic which deserves a place in this paragraph is the *mass transport*. "Mass transport to or from an electrode can occur by three processes:

1. convection and stirring,
2. electrical migration in an electric potential gradient,
3. diffusion in a concentration gradient." [1]

The last process is dominant in mass transport in electrochemical cells, thus is the most notable. The mathematical expressions which are used to describe this phenomenon are the Fick's laws (Equation 1.15 and Equation 1.16).

$$q = D \frac{\delta C}{\delta x} \quad (1.15)$$

$$\frac{\delta C}{\delta t} = D \frac{\delta^2 C}{\delta x^2} \quad (1.16)$$

Where:

**q** is the flux crossing the plane;

**x** is the distance from the plane;

**D** is the diffusion coefficient;

**C** is the concentration.

It is worth to say that also point 1 and 2 have some important implications. The convection and stirring can be used to move electroactive species to reaction sites. While the migration effects could cause anomalous dendrite formations and growth, which in turn lead to the failure of the cell by short-circuit.

### 1.3 State of the Art

In the last century many improvements were achieved in battery technology (Figure 3), both through incessant studies and improvements of one specific system and through the usage of new materials and electrochemical systems. [1]

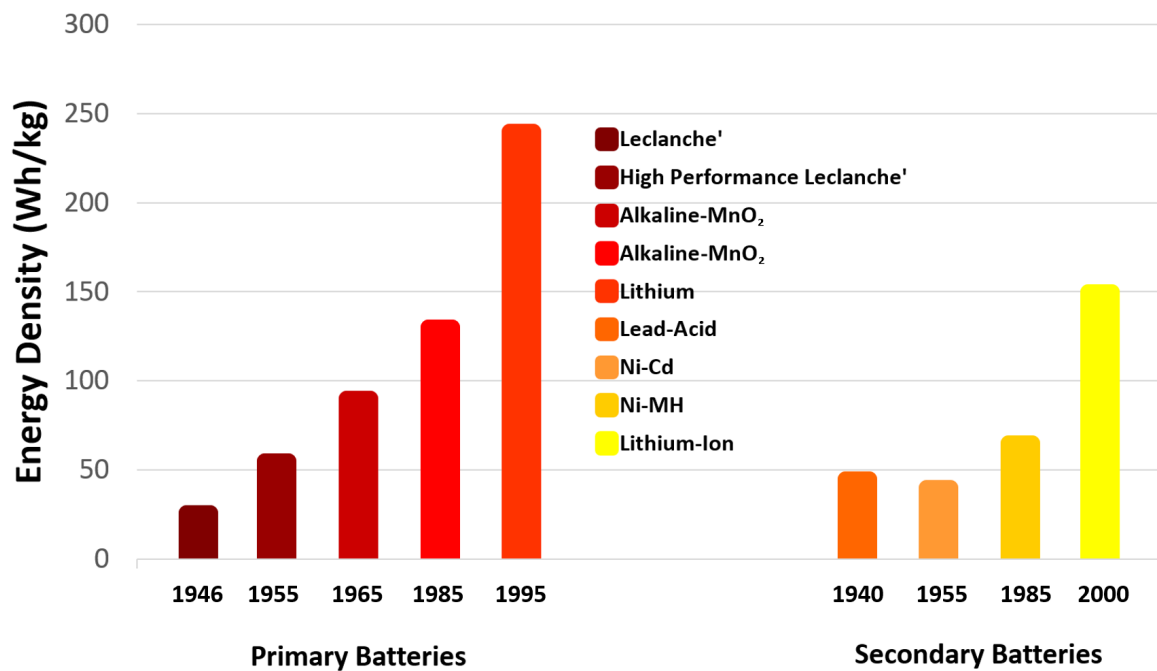


Figure 3: Commercially available batteries advances through time.

The values of specific energy showed in the graph above are actual data, obtained from real experimental tests on batteries. Other two parameters usually used in the literature are the theoretical specific energy, which consider just the active materials and the theoretical specific energy of a practical battery, which takes into account also the non-reactive components of a battery.

Thanks to a high specific energy, better coulombic efficiency and astounding cycle life compared to his competitors, Lithium-ion batteries conquered the market and are now the power source for quite all electronic portable applications.

The highest energy density achieved today from a Li-ion system is 365 Wh/kg, the cycle life could be more than 1000 cycles, and the operating temperature range is  $-30^{\circ} \rightarrow 50^{\circ}\text{C}$ . Moreover recently a new Lithium system has been explored, the Lithium-Sulfur, that with a theoretical energy density of 2600 Wh/kg bode to be part of the next generation of batteries. In this paragraph I do not consider yet the metal-air batteries, which have energy densities in the astonishing range of 3000–5000 Wh/kg, but they are still some years far from been commercialized.

## CHAPTER 2

### METAL - AIR BATTERIES

#### 2.1 The Future of Energy Storage

Battery evolution is targeting always smaller and lighter systems in order to keep up electronics development. Electric vehicles are starting to spread in many countries and several multinational car corporations, captained from Tesla, are investing on this technology. Moreover it will be just a matter of time before also the electric grid would need powerful batteries to implement the renewable energies, overcoming the problem of discontinuous production.

Venkat Srinivasan claimed, in a conference at UC Berkeley, that a "Moore's law" for batteries could be defined: each year the energy density undergo to an improvement of the 5%. This was true in the last years and it is referred to the commercially available systems.

The two main trends that are needed for battery evolution are:

1. Increase in energy density [Wh/kg];
2. Decrease in cost [\$/kWh].

Right now, with Li-ion systems we are in the range of 600 – 400 \$/kWh and an energy density up to 200 Wh/kg, which means an EV with a range of around 200 miles with a cost of the battery pack approximately of \$30000, i.e. the price of an entire gasoline-powered car. [2] The Department of Energy goal is to reach within 10 years an average cost of 100 \$/kWh with an energy density of 900 Wh/kg, which would correspond to an EV with 350 miles of autonomy.

At first it could seem an incredibly optimistic target, but scaling and vertical integration of EVs in the next 5 years is expected to dramatically reduce costs. As far as concerns the performance that will be required from a battery, it is unthinkable to lie on the Li-ion systems for a long time. It will be soon reached the maximum exploitation of that kind of battery, as I already mentioned, and also that will not be even close to be a good candidate for the applications of the future.

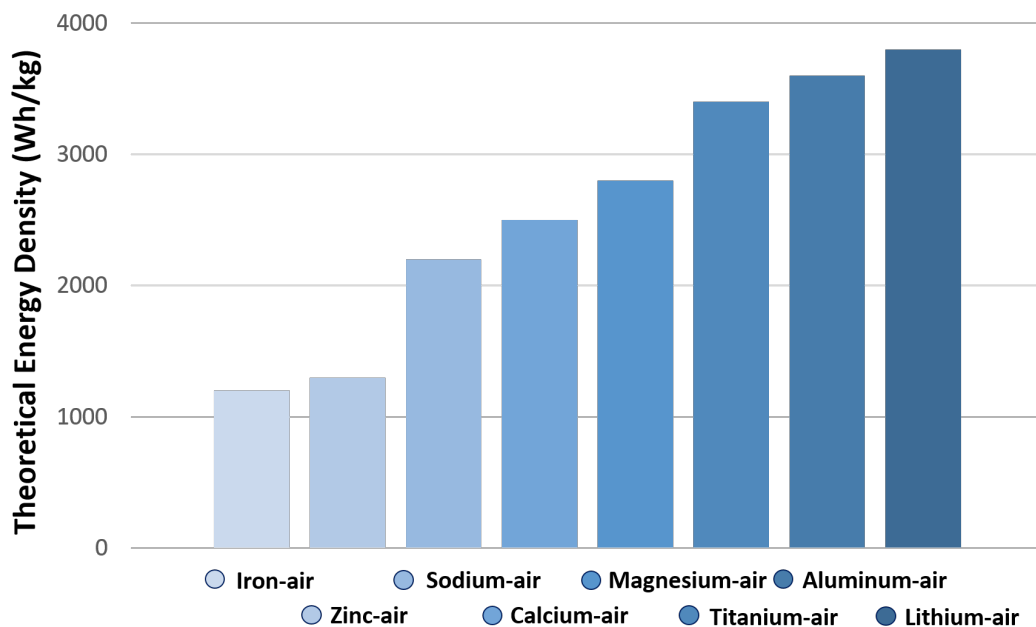


Figure 4: Theoretical gravimetric energy densities of Metal-air systems.

Metal-air batteries are considered from the great majority of scholars in the energy storage field to be the future of batteries. The principal attraction of metal-air systems is the impressive theoretical energy density (Figure 4), which is on average around 10 times higher than the one of Metal-ion batteries and just a little bit lower than the one of gasoline if we consider the

practical applications.

It is worth saying that the practical energy densities range approximately between 1000 – 2000 Wh/kg, which anyway is 5 to 10 times higher than the practical values for Li-ion batteries.

Hence, eventually, why will we need Metal-air batteries in the near future?

First of all, **Electric Vehicles**. The first EV to be sold was the "EV1", produced by General Motors during the nineties. It was welcomed with great pleasure from consumers and it seemed to be the beginning of a revolution for the road transport. As we know that shift did not happen in that period and the reasons why go a little bit off topic for this thesis; so let's just say that it was not the proper period and that there were big interests in stopping that project. Anyway, some years later, (2006, California) a novel car company, founded by a young dreamer, presented the first totally electric vehicle, the Tesla Roadster. This was actually the beginning of that revolution which GM could have started 20 years before.

Tesla ideas rapidly gained the public approval and Carlos Ghosn, the CEO of Renault-Nissan Alliance since 2001, caught the importance of what was happening and invested on Li-ion, making EVs the heart of their future plan. The economical crisis slowed down the process, yet in the 2010 the "Nissan Leaf" was presented, the first mass EV, with minor quality but also lower price than Tesla models.

In the next years all the automotive colossi began to develop electric, or at least, hybrid vehicles. The Department of Energy forecast that within 2015 one million EVs would be sold and the prevision turned out to be quite exact.

At present Tesla is leading the market of EVs. The Tesla "Model S" has a range of 480 km per single charge, while the second best EV, the new "Nissan Leaf" could afford just 220 km per charge. However, besides autonomy, there are other two fundamental parameters in the design of a EV's battery pack: the weight and the cost.

Metal-air batteries, if properly developed, could be used to improve all these three aspects, bringing us to a battery pack which is lighter, less expensive and with a longer range.

Certainly there are other important issues to be considered, like the recharging time, the safety and the production of clean electric energy, however the increasing price in oil and the always worse pollution theme suggest that the future of all transportation would be Electric Vehicles and the only way to make it happens more rapidly is to design a proper energy storage system.

The second branches which will require Metal-air batteries are **Electric Grid** and **Renewable Energies**. The grid requires storage at many time scales, from seconds to hours, it needs to be low cost ( $< 100$  \$/kWh), to last more than 20 years and finally to be incredibly safe. Li-ion could not be the solution, since performances well above the intrinsic limits of the system are required.

Another important point to consider in the future is the development of systems to produce renewable energy, which is continuously growing in the last decades. In the 2014 was a bit less than  $1/5^{\text{th}}$  of the world electricity production, but the rate is positive and increasing (Figure 5 and Figure 6).

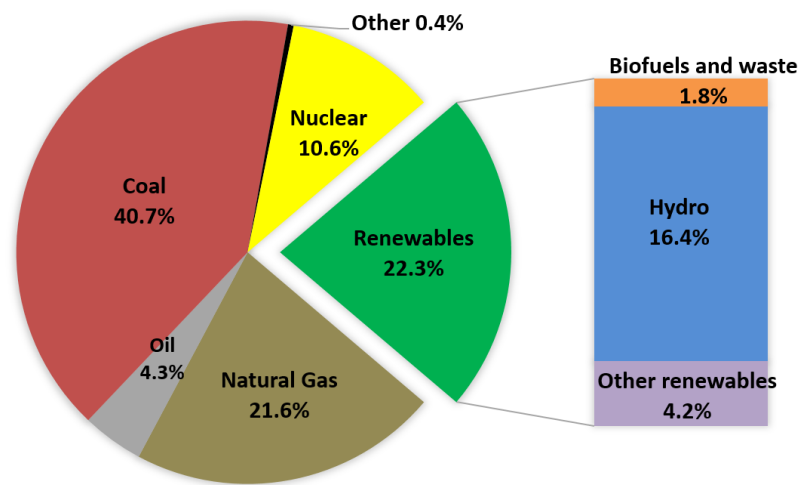


Figure 5: Global electricity production in 2014 divided per source. (Data source: Renewables 2016 global status report)

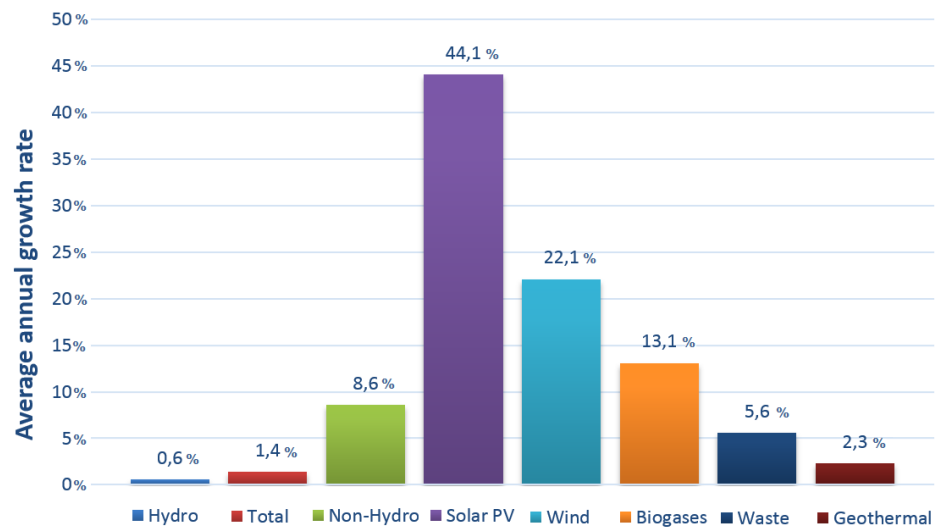


Figure 6: Annual growth rate of electricity production from renewable sources from 1990 to 2015 in OECD countries. (Data source: Renewables 2016 global status report)

The progress in this field seems to lead to a discretization of the production, with millions of little producers, i.e. each household with a wind turbine or a solar panel installed for example, who will help big producers in the energy livelihood of the community. What energy storage could give to renewable is flexibility. The main issue with renewable sources is the discontinuity in production, but with a well designed grid, a comprehensive development of the numerous sources and an efficient, low cost and high energy density storage system we could actually start to think of increasing that  $1/5^{\text{th}}$  to a more charming  $1/2^{\text{th}}$ .

Last, but not least **Portable Electronics** is exponentially growing in volume of production and computative power of the products, requiring always larger source of energy from which draw out. Since now batteries have more or less kept up with electronics, but is difficult to believe that the smart-phone of the future, let's say 10 years from now, could be fed by a Li-ion battery. The "brain" of the electronic devices is improved of two times each 18 months, yet without a "heart" to sustain it, his power cannot be exploited.

Finding new energy storage systems is vital to proceed with the technological development we have been attended during the last decades and this is the leading motivation behind the research on Metal-air batteries.

## 2.2 Outlook of the System

### 2.2.1 General Details

A Metal-air battery exploits the same functional concepts of a ion battery, yet instead of a solid cathode, the substance which undergoes a reduction during discharge is the air, which is purged in the cell at a certain pressure, obtaining a quite inexhaustible reactant source. More specifically, the Oxygen is the only gas we want to reduce theoretically, however all the other gases present in ambient air (i.e. Nitrogen, Carbon dioxide and Argon) plus the water vapor, influence the actual performance of the system.

The great advances in Li-ion batteries and the very high theoretical energy density led the development of Metal-air batteries to start from the Lithium-air system. Therefore the concepts shown in this paragraph are referred in particular to Li-air systems, yet I will try to keep the discourse general, to make it possible to extrapolate these notions for all the other Metal-air systems.

A first parameter to distinguish between different kinds of batteries is the composition and state of the electrolyte. There could be 4 types: non-aqueous, aqueous, hybrid and solid state.

[3] Non-aqueous batteries have proved to be the most promising, thus this system is the one which has been the most investigated and the one we will consider basically from now on.

There are two main assemblies to test a Metal air battery: the coin cell and the Swagelok cell. Regardless the cell chosen the principal components of a Metal-air battery ordered as for the assembly are:

1. Anode

2. Separator
3. Electrolyte
4. Porous Cathode

The **anode** simply consists in a thin coin of metal, similar to ion battery systems. It is the reservoir of metal ions, which go toward the cathode during discharge to form products and it is also where they should return during charge.

The preparation changes accordingly to the kind of metal used, considering the formats commercially available, i.e. cubic or cylindrical chunk, foil or directly coins. However quite all the materials have a common property, being highly reactive with air; thus the preparations must be performed inside a controlled environment, usually using a glove-box.

The **separator** accomplish two key tasks. First of all it avoids direct contact between anode and cathode, which would result in short-circuit. Moreover it is used as selective membrane to block the passage of some unwanted molecules, usually it avoids the molecules present in air to come in contact with the working anode surface.

There are two kinds of separator commonly used: the membrane and the glass fiber. They both could be purchased with different thicknesses and porous sizes, accordingly to the system requirements.

The **electrolyte** is a fundamental component for a battery, it is the carrier used by ions to move from anode to cathode and viceversa. It closes the internal electrical circuit of the cell.

The three main properties of an ideal electrolyte should be: high ionic conductivity, to enhance ions mobility; very low electronic conductivity, to minimize self-discharge, and a great stability,

to avoid decomposition and side products formation.

As I already mentioned, there are different types of electrolyte, yet the most used for Me-air batteries are the non-aqueous. Among non-aqueous electrolytes the most used are the organic electrolytes and we can choose between different families such as ether-based, glyme-based, glycol-based and carbonate-based.

The **porous cathode** of Me-air batteries is the major difference with the Me-ion systems. In an ion battery the cathode firsthand participate in the reaction, in the sense that its molecules undergoes reduction during charge and oxidation during discharge. Differently, in a Me-air cell the cathode main task is to accommodate the reaction. Actually the electrochemical cathode is by definition the air and specifically, in theory, the Oxygen, because is the only specie (besides the metal) which should reduce and oxidize. Despite this, the carbon-based porous electrode which give hospitality to the molecules to react is in practice called cathode.

The essential property of the cathode is the porosity, since higher porosity means higher surface and in turn, more rooms for the reaction to happen. The most used cathodes are carbon-based with a gradient of porosity (normally the higher porosity surface facing the separator while the lower porosity surface facing the air reservoir). Carbon is preferred among other elements due to the strong covalent bonds between his molecules, which make it a more stable environment and this is fundamental, as for the electrolyte, to minimize atom detachments and in turn side products formation.

In order to facilitate the reactions, catalysts are often used in the cathode. They decrease the energy required from the reaction to start, creating active sites within all the cathode and

particularly in the region of high porosity.

### 2.2.2 Main Challenges

Metal–air batteries are still under research and it will pass a while before we could see them scratch the hegemony of the Li–ion system on the market. The challenges which still are waiting to be solved are numerous and will require other few years of deep study.

First of all I always referred to those systems as Me–air batteries, yet actually the great majority of the systems developed so far are Me–Oxygen batteries. The air, as everyone knows, is made by different components, the problem is that we want just the Oxygen to participate in the electrochemical reactions but since the other species do not want to accept our will, a few side–reactions usually happen and those lead to a degradation in performance and a reduction in battery life. In order to simplify the system and concentrate the efforts on other issues, instead of purging ambient air, just pure Oxygen is often used.

Therefore the first big challenge is passing **from Me–Oxygen to Me–air** batteries. Nitrogen and Argon are stable and do not easily participate in the reactions, while many effects come from the other impurities: Carbon dioxide and Water vapor. Both  $\text{CO}_2$  and  $\text{H}_2\text{O}$  react with the species present in the system during discharge, forming different kinds of side–products. These products require usually more energy to be dissolved during charge, so they increase the overpotential of the cell, reducing the efficiency of the system. Another worse scenario is that these reactions are irreversible, which means that once formed, those side–products will remain on the cathode, occupying active sites and favoring clogging till the death of the cell.

Other consequences are reported but are not yet well explained, for example adding trace quantities of water seems to increase the capacity of the system and to affect the products' growth in shape and size; while to some extent  $\text{CO}_2$  combined with  $\text{O}_2$  boost the capacity and the stability of the system. [3]

As far as concerns Lithium batteries, a special treatment to create a passivation layer on the anode surface (i.e. Solid Electrolyte Interface, SEI) has been designed. This stable film was studied to prevent further reactions between the anode and the electrolyte, but it resulted to be suitable also to improve the performance of the battery in ambient air.

The second big challenge is to highly improve the **stability of electrolyte and cathode**. One of the principal cause of performance degradation and ultimately of cell death is exactly the instability of electrolyte and cathode. The reaction of electrolyte and cathode with the species in the cell lead to the formation of side-products, with all its negative results such as clogging and an increased resistance of the system. This bring to an increment in the overpotential which in turn facilitates the progress of other side-reactions and so on, in a vicious circle. Thus, a stable cathode need to be designed, an electrolyte which is not prone to react with it should be found and finally a method like SEI formation through passivation should be introduced to protect the anode.

Another considerable issue is **understanding the mechanisms of the reactions**. Many studies have been performed on this topic and lots of hypothetical reaction paths have been reported, yet is quite impossible nowadays to practically prove which is the closest to reality. There are essentially two approaches to face this issue. The first is funded on chemistry and

energy studies on the species of the system, while the second is based on computer simulation and molecular dynamics modeling. Both methods requires highly specialized people and a considerable amount of time and, beyond that, the results hardly are completely reliable.

The last big challenge to ameliorate the Me-air systems is the **development of a Oxygen selective membrane**. [4] The design of such a membrane could directly solve the first issue disclosed in this paragraph (i.e. passing from Me–Oxygen to Me–air) and would be a great jump toward the commercialization of Me-air batteries.

Moreover an highly selective membrane could also be used as separator, avoiding anode contamination (for example Oxygen–crossover) and in turn enhancing the performance and stability of the cell.

## **2.3 Chemistry & Energy of Developed Batteries**

### **2.3.1 How to choose between metals**

As I outlined in the previous paragraph, Li–Oxygen, thanks to its incredibly high theoretical energy density, attracted most of the researchers; in fact lots of studies were performed on this system and hundreds of papers were published during last decade. However the challenges to be overcome proved to be tougher than expected and after many years of study the development of a highly reversible Me–air battery remains a target.

That is why over the last period many other alternatives to Lithium have been analyzed. Different metals have been studied and used to create new Me–Oxygen systems and among these some promising competitors to Lithium raised.

TABLE I: COMPARISON OF PRINCIPAL PARAMETERS FOR A ME-AIR BATTERY'S ANODE.

Anode	Main Discharge Product	Theoretical Potential [V]	Theoretical Energy Density <sup>a</sup> [Wh/kg]	Cost [\$/kg]
Lithium	$Li_2O_2$	2.96	3800	68
Sodium	$NaO_2$	2.27	2200	1.7
Magnesium	$MgO_2$	2.91	2800	2.75
Aluminum	$Al_2O_3$	2.71	3600	1.75
Potassium	$KO_2$	2.48	1000	20
Calcium	$CaO_2$	3.38	2500	200
Iron	$Fe_3O_4$	1.28	1200	0.40
Zinc	$ZnO$	1.65	1300	1.85

<sup>a</sup> Based on the total discharge product weight.

Different features need to be taken into account to find a valuable alternative, as we can see from Table I. The first key parameter is the **energy density**. It is clear that the Lithium has by far the highest theoretical value, such high that is comparable with the one of gasoline. However we should also consider the practical value, which is around 3600 Wh/kg (again very close to the one of gasoline). It is still two, or in some cases three, times bigger than the competitors' values, but the distance is way reduced. Another practical consideration is that the actual batteries commercially available are Li-ion and, as we saw, have energy densities around 250 Wh/kg; thus even a system with 1000 Wh/kg would be a big improvement. Farther, the best practical usage of gasoline for automotive applications is around 1700 Wh/kg. [5] Therefore there are no real motivations to not try to find a system with new materials, which could prove to have great performances in terms of cyclability, efficiency and cost, besides grand energy density.

Other two important variables that must be considered, if we want to be provident and pragmatic, are the **earth's crust abundance** of the elements and the **cost**, which are normally related. In a scale, the estimated percentage of Earth' crust filled from each metal reported in Table Table I, would be as follow: Aluminum (8.13%), Iron (5.00%), Calcium (3.63%), Sodium (2.83%), Potassium (2.59%), Magnesium (2.09%), Zinc (0.0075%), Lithium (0.0018%).

It is evident that the abundance is not directly proportional with the cost. The difficulty of the extraction of each element here plays an important rule and also the economic demand of the product has notable consequences.

Briefly, the best choices of metal anodes as far as concerns a balance between cost and Earth abundance are Iron and Aluminum, followed by Sodium and Magnesium. Then the exceptions Calcium and Potassium, that besides a widespread presence on Earth have considerable costs, and on the other side Zinc which has a competitive cost but is a quite precious resource on Earth and thus could difficultly be the main component of mass batteries. Finally there is Lithium, that in this particular ranking is at the last position, since the cost of the material is pretty high and the Earth abundance is really low.

The last feature we account is the **energy efficiency** of the system. This is a debated topic in the electrochemical field in general and there has not yet been found a proper definition for Me-air systems. I will just report the most used formula of efficiency (Equation 2.1) in the battery literature, which is the one valid for Li-ion system.

$$\eta_{co} = 1 - \frac{\text{Charge Pot.} - \text{Discharge Pot.}}{\text{Charge Pot.}} \quad (2.1)$$

Apart from the validity of the formula, the concept that emerges is that the main value to consider is the polarization gap, i.e. the difference between the charging overpotential and the discharging one.

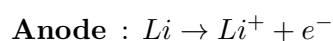
The overpotentials of a battery are strictly related to the nature of the reactions and in turn to the products of the discharge. Following this route it is clear that the more complex the product is, the more difficult would be to form and also to dissolve it. What makes a molecule complex is obviously the number of atoms, but also the number of electrons involved in the reaction of formation/dissolution. In this sense superoxides are better than peroxides. They are simpler and kinetically favored by the fact that just one electron needs to be transfer in order to have the reaction. That is the reasoning behind the great consideration relied on Sodium at the forefront and Potassium next.

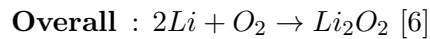
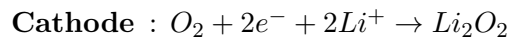
### **2.3.2 Overview on the present of Me – O<sub>2</sub> batteries**

As we saw in the previous paragraph, numerous aspects must be taken into account for the choice of a new anode and this gave rise to many valuable Me – O<sub>2</sub> systems. The aim of this section is to briefly comment each of the main systems reported in literature. Here I will not deal with Na – O<sub>2</sub>, since it will be the main character of the next chapter.

#### **Lithium–Oxygen**

The theoretical discharge reactions of the cell are:





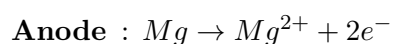
Thus the main product formed is lithium peroxide,  $Li_2O_2$  (theoretical potential 2.96 V). [7] Although, other species were found analyzing the cathode after discharging the cell: Li-carbonate compounds (such as  $Li_2CO_3$ ), due to the decomposition of the porous cathode or from carbon-based electrolyte; and Li superoxide (i.e.  $LiO_2$ ), which is from the majority reputed to be the intermediate and instable compound that finally lead to the formation of the peroxide. [3]

The Li –  $O_2$  system is the most developed among the Me –  $O_2$  batteries both for performances and studies. However, before those batteries could be commercially feasible products, still many issues have to be overthrown. From conceiving a proper cathode/catalyst architecture, to optimizing electrolyte compositions and explicating the convoluted reactions occurring during the cycling of the cell. [4][8]

Furthermore, the low abundance on Earth of Lithium and the high price suggest that it could not be suitable for a global low-cost energy storage device, thus other alternatives must be considered.

### Magnesium–Oxygen

The Mg –  $O_2$  system has not yet attracted much attention and few studies are reported. The theoretical discharge reactions are:



**Cathode** :  $O_2 + 2e^- + Mg^{2+} \rightarrow MgO_2$

**Overall** :  $Mg + O_2 \rightarrow MgO_2$  [9]

Thus, Mg is oxidized to  $Mg^{2+}$  and two electrons are transferred to the cathode.

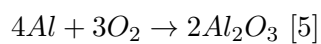
The main issues with Magnesium are related to his high polarization and low efficiency. [10]

Magnesium-based batteries have been for a long time considered as primary batteries, as far as Zinc-air, yet recently the reversibility of the system was shown, opening to new studies and more research on this material. [11]

### **Aluminum–Oxygen**

There are some practical advantages from the choice of this metal. As we saw, Aluminum is one of the most abundant element on Earth, the third after Oxygen (46.6%) and Silicon (27.7%) and its cost per kilogram is just 1.75 \$. Moreover other positive aspects are the low equivalent weight of Al-based system and the safety characteristic; additionally the big plus is that Al and its products are not toxic. [5]

The specific reactions on anode and cathode are not yet clear, while the total cell reaction has been postulated has:



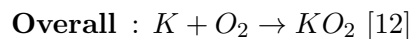
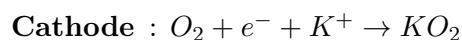
For now, very little has been published on this topic and the system still remains irreversible. However, with deeper studies, it is possible that a reversible system will be designed, as it happened for Magnesium.

### Potassium–Oxygen

The Potassium is, as well as Sodium, the metal which is attracting always more attention in the last years.

It is an abundant element and also if the price is not exactly economic, it still costs more than three times less than Lithium. Anyway the actual fascinating property is the theoretical high efficiency of the system. Potassium, like Sodium, produces superoxides during discharge. This lead to superior reversibility and lower overpotentials, with polarization gaps which are 10 times less than the one of Lithium batteries (0.1 V versus 1.5 V).

The theoretical discharge reactions are:



One of the main challenge for Potassium is enhance the anode stability. Proper combination of an ether–based electrolyte and salt ( DME with KTFSI) is reported to work in the right direction to solve this issue. [13] Another drawback of this system is the high reactivity of Potassium with ambient air, especially with water, and the toxicity of his products. Those make the safety of the system pretty low and it is an issue that must be solved in the future.

However the performances are promising and superoxide–based batteries are encouraging always more research, thus K – O<sub>2</sub> system will continue rapidly its development.

### Calcium–Oxygen

Very recently the feasibility of Calcium deposition using organic electrolyte was demonstrated and also the reverseability of this process was shown, marking the first step toward the design of a new rechargeable battery. [14]

Other studies were performed but it is still unclear which is the main product during discharge among three candidates:  $\text{CaO}_2$ ,  $\text{Ca}(\text{O}_2)_2$  and  $\text{CaO}$ . [15]

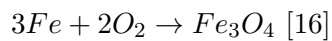
Calcium is abundant in the continental crust, yet it is very expensive, three times more than Lithium, and there are apparently no advantages that counterbalance its price, thus it seems difficult that lots of effort will be placed on this system for now.

### Iron–Oxygen

The earlier research on Iron–air battery was performed by NASA more than 40 years ago, but it never resulted in a practical application. Recently, with the new wave of interest for the Me–air systems, the Iron has been revalued as a possible anode material.

Iron is the metal with the lowest price among the others analyzed in this paragraph, its production and recycling is well established all over the world and it is one of the most abundant metal on Earth.

The simplest overall cell discharge reaction can be written as:



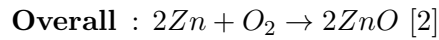
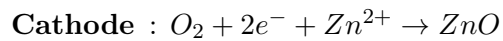
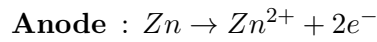
The reversibility of this system has already been proved and high cyclability shown. However the low open–circuit potential and efficiency are negative aspects that need to be taken into

account. Thus big improvements are required to make this battery live up to other competitors.

### **Zinc–Oxygen**

Zinc–air battery exist as primary battery from over a century and they can potentially be manufactured at very low cost, about two orders of magnitude lower than Li-ion. As for Iron, the increasing necessity for a powerful energy storage system led to a renewed interest in this system and studies on  $\text{Zn} - \text{O}_2$  has been performed in the last years.

The main theoretical discharge reactions are:



Traditionally, Zinc–air are non-rechargeable and known for the high energy density, yet the limited power density restricted the application's range of this system to a niche market (for example hearing aids). Lately progresses have been made toward high power density and electrical rechargeability, which could start a revaluation of this system.

## CHAPTER 3

### SODIUM - OXYGEN BATTERY

#### 3.1 Introduction

##### 3.1.1 General Characteristics

Sodium is a chemical element with atomic number 11. It is a soft and silvery-white metal, to be more accurate it belongs to the family of alkali metals (i.e. group 1 of the periodic table), since it has just one electron in its outer shell.

From this arises its high reactivity, having just one electron of difference from the extremely more stable configuration of Neon (noble gas), it tends to donate this "extra" negative charge to other species. In fact the free metal does not occur in nature, yet Sodium appears in numerous minerals and salts.

It follows that the first ionization energy is low (495.8 kJ/mol), while, in contrast, the energy required to bring away a second electron is very high (4562 kJ/mol). That is why the common oxidation state of Sodium is +1, and so the ordinary cation  $\text{Na}^+$ . To make a comparison with other alkali metals, in general, Sodium is less reactive than Potassium but more than Lithium. Sodium melting point is 98°C, while the boiling point is 883°C; those values are lower than the ones of Lithium but higher than the ones of heavier alkali metals, such as Potassium. At standard pressure and temperature sodium is a soft material and could easily be cut and pressed. One issue is the high reactivity with Oxygen, which oxidizes its surface quickly, forming a gray-

ish white layer of sodium oxide ( $\text{Na}_2\text{O}$ ). Thus pure sodium, which is prepared from compounds, is usually stored immersed in oil or inert gases. This is fundamental to avoid dangerous situations, since Sodium spontaneously explodes in the presence of water and also just a contact with mucous membranes or eyes can cause severe burns.

As far as concerns production, pure Sodium is employed in rather specialized applications and around 100,000 tonnes are produced annually. As we saw Sodium is commonly found as compound on Earth and the most ordinary one is the  $\text{NaCl}$  (i.e. the cooking salt). In fact pure Sodium is nowadays made through electrolysis of molten sodium chloride.

### **3.1.2 Why Sodium could be better than Lithium?**

In the Paragraph 2.3.1 we analyzed the main properties to take into account to choose between different metal anode candidates. Now I will try to explain the advantages in choosing Sodium instead of Lithium.

The first parameter which encouraged researchers to find alternatives to Lithium is the scarce Earth's abundance of that element. We saw that Li is just the 0.0018% of Earth's crust and the gradual depletion of the last years, due to its utilization in the energy storage field, is contributing in enhancing the price more and more. On the other side there is Sodium which is the sixth most abundant element on Earth (2.83%), which in practice is more or less 1500 times more abundant than Lithium. If the final goal of the Me-air research is to unseat the Li-ion batteries and to revolutionize the energy storage field, an enormous quantity of the anode component will be required. Thus, it seems a reasonable choice to replace the anode material

with a more abundant one.

The second property, related to the first one, is the price. Lithium metal costs about 68 \$/kg while pure Sodium 1.7 \$/kg. The difference, also here, is remarkable and it is not just a matter of the anode, yet also of the salts used in the systems. It is true that the most expensive components of a battery are the electrolyte and the catalyst, however also salt and anode give their contribution.

Thus Sodium is way more abundant and a lot less expensive than Lithium.

Anyway these are not the only reasons behind the interest on Na – O<sub>2</sub> batteries. An important factor is related to the product formed during discharge. As I already briefly disclosed, Sodium–Oxygen batteries, as well as Potassium–Oxygen, work on the formation and dissolution of superoxides. This means that the fundamental functioning of the cell resides on a one–electron transfer reaction. Therefore less energy, and in turn overpotential, is required from the system; leading to a high efficiency battery with low polarization gap.

Moreover many scholars were attracted by Sodium due to its similarities with Lithium in some physicochemical properties and in the electrochemistry. From here was deducted that the studies performed on Lithium during all these years could result useful and so that the time–line which should bring to commercialization could be cut.

Unfortunately, these positive expectations have been slowly resized because of many issues encountered into practical systems. However, on the other hand, those similarities effectively helped to speed up the development of the first cells.

The only feature in which Lithium is almost unbeatable is the energy density. The theoret-

ical value for Lithium is 5 times higher than the Sodium one and the practical is still more or less the double. Anyway it is worth saying that the actual values of energy density of gasoline is about 1700 Wh/kg, which is close to the practical value of pretty much all the Me–Oxygen batteries studied so far and that the actual Li–ion batteries can store around 300 Wh/kg.

Thus, also if in general this is a key parameter, it is not the case, relatively to similar systems, in the near future and farther in the majority of the applications.

## **3.2 Reported Studies**

During the last three years the number of academic papers published on Sodium–Oxygen batteries increased exponentially, confirming the growing interest and confidence in this system. The aim of this paragraph is to report the studies which, to the best of my knowledge, could be useful to step in the topic of Na – O<sub>2</sub> battery and to bring some order among the dynamic environment of publications.

### **3.2.1 Product Structure and Characteristics**

#### **3.2.1.1 The Superoxide is Cubic!**

In the late 1950 the first study on "The Crystal Structure of Sodium Superoxide" was published. At that time this Sodium compound was just recently "been prepared in reasonably pure state [through] the reaction of Sodium peroxide, the [common] oxide obtained, with Oxygen at 500°C and 300 atm pressure". [17]

The samples prepared in this manner were different mixtures of peroxide, superoxide and hy-

drate products and just the one with 70% of  $\text{NaO}_2$  showed a cubic phase after powder diffraction, while the others had many complicated patterns. From this observation Templeton and Dauben deduced that the cubic phase concided to Sodium superoxide. Proceeding with studies and calculations they conclude that the actual structure of  $\text{NaO}_2$  is a face-centered tetragonal lattice of  $\text{Na}^+$  interpenetrated "by a similar face-centered lattice of  $\text{O}_2^-$ , to form a distorted NaCl structure". [17] One issue is that to maintain a "face-centered symmetry the Oxygen pairs must have [a] disordered orientation" and that is difficult to define the most favorable arrangement. [17]

However they could compute that the Sodium superoxide face-centered cubic structure has an edge of 5.49 Å and that the bond distance of superoxide ion (i.e. O-O) is 1.33 Å; finally they also observed that, if exposed to ambient air, this ordered structure was rapidly destroyed, a topic that we will face later.

A subsequent study (1953) on the stability of Sodium superoxide structures at different temperatures pointed out that above  $-50^\circ\text{C}$  (i.e. also at room temperature)  $\text{NaO}_2$  is stable in the cubic structure cited before, while at lower temperatures different and more disordered lattices seem to be preferred. [18] Interestingly was also observed that the disorder in the Oxygen pairs is likely to be dynamic at room temperature.

More recently other studies were performed on the Superoxide structure, as product of Sodium-Oxygen batteries. Many different arrangement of the four superoxide ions along the cell diagonal within the pyrite unite cell were modeled and computed. The result was that the difference in energy of the configurations was in a small range up to 150 meV/formula unit and hence

from a thermodynamic point of view was concluded that could be possible to have all these combinations at room temperature. [19]

### 3.2.1.2 Superoxide or Peroxide?

One of the most debated topic on Na – O<sub>2</sub> batteries regards the products.

The first big issue is to understand whether we are discharging Sodium superoxide (NaO<sub>2</sub>) or peroxide (Na<sub>2</sub>O<sub>2</sub>).

In non-aqueous Li – O<sub>2</sub> cells is quite defined that Lithium peroxide is the only discharge product, while for K – O<sub>2</sub> cells the Potassium superoxide is claimed as the sole product. Unfortunately, Sodium seems to be a borderline case and in turn the situation is more complicated. Some groups reported the formation of the superoxide and so a one-electron transfer, while others argued that they had the formation of the peroxide and a two-electron transfer.

Let's face the problem with order. From the thermodynamic point of view, Sodium peroxide seems the more stable at standard conditions, since it has a free enthalpy of formation of  $\Delta G_f(\text{Na}_2\text{O}_2) = -437.5 \text{ kJ/mol}$ . On the other hand, the superoxide formation is energetically close ( $\Delta G_f(\text{NaO}_2) = -437.5 \text{ kJ/mol}$ ), but still 12 kJ/mol lower. Moreover, this same little difference is showed also in the standard open cell potentials, respectively  $E(\text{Na}_2\text{O}_2) = 2.33 \text{ V}$  and  $E(\text{NaO}_2) = 2.33 \text{ V}$ . Obviously the solution is not that simple and many factors have not yet been considered. "The difference in the free enthalpies of formation of bulk Na<sub>2</sub>O<sub>2</sub> and NaO<sub>2</sub> is less than 3% and probably smaller than the error margins of the thermodynamic data", thus it is difficult to make some deductions from these values. [20]

Other theoretical studies were carried out considering the effect of dimension and kinetics. Lee et al. concluded that, under standard conditions, the Sodium superoxide is favored and thus more likely to form, since the one-electron transfer required for its reaction is kinetically favored. [21] In contrast Kang et al. claimed that the more stable product under standard conditions is the peroxide in the bulk phase; however considering the crystal size they demonstrated that  $\text{NaO}_2$  becomes more stable for crystals under 6 nm of diameter. [22]

Therefore we can conclude that theoretically the formation of the Superoxide is predominant respect from the one of Peroxide, still remembering that the available data lack a bit of accuracy.

The main problem with theory is that it not always reflects practice. Charge and discharge hysteresis of cells, usually reported as potential vs. capacity, contains both kinetic and thermodynamic information. In charge/discharge characteristics there are two potential plateaus, which correspond to specific reaction equilibrium during the two working phases of the battery. These two potentials should be close to the theoretical value but have also overpotential contributions from different processes (see Paragraph 1.2.2).

The point is that the potential's characteristics reported are reasonable referred to the product claimed to be formed. All groups which stated the formation of the Superoxide  $\text{NaO}_2$  reported flat discharge plateau for both discharge consistent with a one-electron transfer reaction. On the other hand, reports on Peroxide  $\text{Na}_2\text{O}_2$  as main discharge product show higher overpotentials and polarization gap up to 2 V. Actually that is not all, other researchers evinced the formation of a hydrated form of peroxide as principal product ( $\text{Na}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ ) and reported

characteristics which are similar to the Superoxide ones initially, but then a gradual increase in the potential gap makes them behave as if the product is a Peroxide. [20]

Thus, from the practical point of view, different products seem to be formed and dissolved.

How could we explain this divergence between practice and theory?

Let's try to analyze the situation, there are three main points to be considered:

1. if the  $\text{NaO}_2$  undergoes air exposure it is rapidly converted into  $\text{Na}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$  (as they already saw in the 1950);
2. it is difficult to say if the sample would be stable during measurements, for example has been proved that  $\text{NaO}_2$  is reduced to  $\text{Na}_2\text{O}_2$  by electron beam irradiation and though is not possible to use TEM; [20]
3. it is very tricky to differentiate superoxide from hydrated or non-hydrated peroxide species, thus may occur that some results reported were wrong or at least not precise.

In conclusion, both Superoxide and Peroxide (specially hydrated) are reported as discharge products. Anyway, the  $\text{NaO}_2$  has been identified more times without doubt using Raman spectroscopy and its formation's steps have been determined and confirmed. While the  $\text{Na}_2\text{O}_2$  identification appears to be more difficult and easily subjected to inaccuracies, in fact not only is tricky to distinguish between hydrated and non-hydrated forms but also the reaction paths behind the formation of these products remain unclear.

### 3.2.1.3 Intrinsic Conductivity of Discharge Products

Some scholars addressed the intrinsic electronic conductivity of the products as one possible explanation to the difference in performance of Superoxide versus Peroxide systems. In other words, they suggested that the superoxide was conductive, while the peroxide acted as insulator.

Unfortunately this explanation was demonstrated to be erroneous by one study performed by Yang and Siegel. They computed the formation energies and concentrations of different charge-carriers in order to predict the intrinsic conductivity of  $\text{Na}_2\text{O}_2$  and  $\text{NaO}_2$ .

Surprisingly they found out from their calculations that "both Peroxide and Superoxide are wide gap insulators, with bandgaps of 6.65 and 5.30 eV respectively." [23] As far as concerns the Sodium peroxide, many similarities with Lithium peroxide were discovered. "Hole polarons on Oxygen dimers and negative Sodium vacancies [were] identified as main charge carriers in  $\text{Na}_2\text{O}_2$ " and both electronic and ionic conductivity results to be essentially the same for the two different peroxides. [23]

On the other hand transport phenomena in Superoxide is more complex and not yet well studied. Electron and hole polarons concur quite equally to the electronic conductivity of  $\text{NaO}_2$ , while the ionic conductivity "is mediated by a mixture of negative Sodium vacancies and positive Oxygen dimer vacancies". [23] From calculations come out that the electronic conductivity of the Superoxide is just marginally greater than the one of the Peroxide and so, it stays little in general. Instead the ionic conductivity of  $\text{NaO}_2$  is estimated as 10 orders of magnitude higher than the one of  $\text{Na}_2\text{O}_2$ .

This important difference in the ionic conductivity is addressed to intrinsic defects in the Superoxide structure. Calculations suggest that there are three main ionic charge carriers: "negative sodium vacancies, positive oxygen dimer vacancies, and positive sodium interstitials". [23] "These have formation energies [...] approximately 0.5 eV smaller than those of the lowest energy defects in  $\text{Na}_2\text{O}_2$ ", which suggests that the concentration of defects in the Superoxide structure is higher than the one of Peroxide (equilibrium concentrations of defects 8 orders of magnitude higher). [23]

Therefore we are sure that the difference in performance of the two possible products are not attributable to the electronic conductivity, still is not clear if the ionic conductivity is the key to solve this question and farther, also if it effectively is, the "how" remains.

### **3.2.2 Instability and Side-Products**

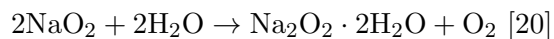
One critical factor in battery systems is cell stability, namely the stability of the main product, which should be Sodium superoxide in the cell ambient. In order to perform this study, different approaches has been taken.

One group ran three cells for the same capacity and with the same current density but with different resting period, showing an increased irreversibility of the reactions proportionaonal to the waiting time. [24] In order to understand better this trend, they characterize two new cells, one right after discharge while the other after 30 hours of resting period. The first difference was in from the SEM micrographs of the cathode, since the first cell showed the widely reported  $\text{NaO}_2$  cubes, "with smooth faces and edges of 5–10  $\mu\text{m}$  length"; while the other cell's morphology of

the products was more "ruined", with rough cubes' surfaces. [24]

The other significant difference was the Na/O ratio. They observed an increase in the Na content from 10.5% to 20.2% and a decrease in the Oxygen level from 14.1% to 5.8% during the resting time. They claimed that the change in the Na/O ratio is attributable to chemical reactions of the discharge product. [24] However is difficult to identify the precise reaction or group of reactions which caused this increase in the Na/O ratio, which could be not just  $\text{NaO}_2$  becoming  $\text{Na}_2\text{O}_2$ , but also the formation of other side-products such as  $\text{Na}_2\text{CO}_3$  or  $\text{NaOH}$  from the reaction of the superoxide with the electrolyte or the carbon cathode. Interestingly, performing a detailed study with Raman spectroscopy, they also confirmed the difficulty to understand the reaction path which lead to the formation of peroxide compounds. They detected a peak at  $1136\text{ cm}^{-1}$ , also found by with Ortiz-Vitoriano et al. after exposing the cathode to ambient air and that was ascribed to the presence of  $\text{Na}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$  from the reaction of  $\text{Na}_2\text{O}_2$  with water. [25] This explanation made sense for them, since they reported also the formation of  $\text{Na}_2\text{O}_2$ , confirmed by the Raman spectra, i.e. peaks in the range of  $750\text{--}800\text{ cm}^{-1}$ . The problem was that just Superoxide was detected in this case and so that band at  $1136\text{ cm}^{-1}$  could not be attributed to  $\text{Na}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ , so they concluded that their peak was due to the presence of  $\text{Na}_2\text{CO}_3$ .

On the other hand, some previous studies and thermodynamic calculations showed that the formation of hydrated-peroxide from superoxide is possible through the reaction:



However "a significant amount of water is required for this reaction", so it is not possible unless

large quantity of water could be decomposed from the electrolyte used. Thus it is unclear which is the responsible for the Raman peak at  $1136\text{ cm}^{-1}$  and also how this product is formed.

Another study confirmed the morphological changes in the discharge products increasing the resting period: from perfect cubes to smudged one and finally to rod-shaped microparticles. [26] At the same time they showed a decrease in the Raman peak attributed to  $\text{NaO}_2$  and an increase in the one they claimed to belong to  $\text{Na}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ . They did not expose the electrode to ambient air, therefore they proposed a dissolution and ionization mechanism which could explain the formation of the hydrated-peroxide from the superoxide. The two key events of this process are the dissolution of  $\text{NaO}_2$  in the electrolyte and the presence of  $\text{H}^+$  ions delivered from the electrolyte.

Summing up, it has been proved that Sodium superoxide is unstable in the cell environment, yet it is still unclear which final products are generated from its instability ( $\text{NaOH}$ ,  $\text{Na}_2\text{O}_2$ ,  $\text{Na}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ , or  $\text{Na}_2\text{CO}_3$ ) and which reactions govern these possible transformations. However, from another perspective this could give a possible explanation to the difference in results reported so far. It is a possibility that just the systems showing low polarization gap and production of Superoxide were working properly, while in the others side-reactions and instability could have led to rapid formation of peroxides or other side products. Then the results were associated with production of just or mainly Sodium Peroxide, yet without being aware of the real composition of those species.

In fact has been recently suggested that the main factor which leads to the formation of Peroxides is the amount of water in the system, that in turn depends from how the Oxygen is

introduced in the battery, i.e. static or flowing conditions. [27] The formation of either  $\text{NaO}_2$  and  $\text{Na}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$  with the same system was performed under controlled conditions and the increased amount of water resulting in the formation of  $\text{Na}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$  in the flowing system was addressed simply to leakages of the frequently used plastic tubing.

Thus, the group mentioned above, substantially claimed that all the reports showing peroxides formation were actually working with  $\text{Na}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$  due to "high" amount of water in their systems, farther they showed that limit the upper potential to  $\leq 3$  V significantly decrease side-reactions and formation of side-products like  $\text{Na}_2\text{CO}_3$ .

In conclusion, the fact that the presence of dehydrated peroxide in a  $\text{Na} - \text{O}_2$  battery is improbable has been recently strengthened by a study on possible reaction paths that could lead to the formation of  $\text{Na}_2\text{O}_2$ . Janek et al. proposed and tested three approaches:

1. electrochemically convert the initially formed  $\text{NaO}_2$  in  $\text{Na}_2\text{O}_2$  under inert gas by continuing the discharge further;
2. load the carbon cathode with  $\text{Na}_2\text{O}_2$  artificially and then use it to cycle a battery;
3. dissolve  $\text{Na}_2\text{O}_2$  in the electrolyte up to saturation. [28]

They combine different characterization methods and analysis (i.e. XRD, Raman, SEM, Charge/Discharge cycling) and they interestingly showed that in all experiments the discharge always drove to the formation of the sole  $\text{NaO}_2$ . [28]

### 3.2.3 Discharge and Charge Reaction Paths

Always more groups are reporting that the effective product of the discharge is Sodium Superoxide, confirming the thermodynamic studies presented above, thus it is becoming clear that, if there are not interference, the only product of a Sodium–Oxygen battery is  $\text{NaO}_2$ . Anyway one fundamental point to understand what is actually happening in our batteries at the nanoscale is to define reaction paths for the formation, deposition and dissolution of the products.

As we saw Sodium Superoxide grows in semi-cubic structures and one interesting point is that they reach dimensions between 5–20  $\mu\text{m}$ , so one order of magnitude bigger than Li–Oxygen batteries' products ( $\text{Li}_2\text{O}_2$ ). Furthermore decomposition of  $\text{NaO}_2$  requires a significantly lower overpotential than Lithium Peroxide. Thus how is it possible than Sodium cells are forming larger particles and they also require less energy to decompose?

Many scholars initially attributed this difference to an hypothetical good electronic conductivity of the Superoxide compared to the Peroxide. Unfortunately, it has been later proved from few studies that the electronic conductivity of  $\text{NaO}_2$  is very low, thus another explanation should be found. A good starting point would be understand the pathway followed by the nucleation and growth of Sodium Superoxide crystals.

Essentially there are two hypothesis:

1.  $\text{NaO}_2$  is formed at the cathode and travels through the electrolyte to the surface of the active sites and nuclei;

2.  $O_2$  is reduced straightly at the  $NaO_2$  crystalline face thanks to the viable, even if very small, electronic conductivity of the Superoxide. [29]

Nazar et al. demonstrated that the first pathway is the operative one and that "it is crucial the presence of a proton phase transfer catalyst (PPTC) to solubilize and transport the Superoxide". [29] They claimed that the proton ( $H^+$ ) could come from any source, such as hydrated salts or directly trace amount of water or also some anhydrous weak acid. The key role in their system was played by the  $H_2O$  radical and they proposed a mechanism of crystal growth here reported.

" $H_2O$  is readily transported in solution to the surface of growing  $NaO_2$  nucleation sites, and deposition is driven by the large negative free energy of crystalline  $NaO_2$ . Kinetics and thermodynamics operate in concert to grow large  $NaO_2$  cubic crystals, giving rise to very high capacities. In the absence of the PPTC, quasi-amorphous superoxide thin films result, which have a very low capacity owing to the low solubility of  $NaO_2$  and/or low conductivity of the solid phase." [29]

Assuming the same mechanism works properly also for  $Li - O_2$  batteries, they explained that the higher potential on charge of those systems is due not only to the formation of stable side products but also and mostly by the fact that  $LiO_2$  is thermodynamically unstable and tends to disproportionate to form  $Li_2O_2$ . The point is that the PPTC works as catalyst also for the charge reaction just for superoxides, thus the peroxide oxidation happens in an uncatalysed and high energy pathway, leading to a higher charge overpotential.

A second study on this topic was conducted by Hartmann et al. some months later and they

also showed that the electronic conductivity of Sodium superoxide cannot be sufficient for the growth of the large particles reported. Therefore they concluded that formation and decomposition of  $\text{NaO}_2$  are governed by a solution-mediated process relying on a soluble superoxide ( $\text{O}_2^-$ ) species. [19]

The solubility of  $\text{NaO}_2$  in the electrolyte has been widely proved, however also the mobility and diffusion of ions in the electrolyte plays an important rule. In fact to keep the overpotential low is necessary that OER sites are located near the  $\text{NaO}_2$  cubes, otherwise  $\text{O}_2^-$  diffusion will limit the reduction rate. [19]

In conclusion, has been proved and then confirmed by many other studies that both discharge and charge mechanisms are dominated by a solution-precipitation route. [30]  $\text{NaO}_2$  forms in the solution and, when/where it locally reaches supersaturation, it start to precipitate and to deposit on the active sites of the carbon cathode. Has been very recently suggested that, as the ORR continues, the electrode becomes covered by always smaller nuclei which could result in the formation of an insulating film-like structure that could lead the further reactions to shift to a surface-process. [31]

What transpires is that kinetics and mobility of ions could be a crucial aspect to be considered in the  $\text{Na} - \text{O}_2$  batteries, however more research on which parameters and conditions enhance or limit this solution-mediated process must be completed.

### 3.2.4 Current Dependency of Shape, Size, and Distribution

One interesting point recently confirmed in Sodium–Oxygen batteries is the dependency on current rates of shape, size and distribution of products. The growth and dissolution mechanism reported above, i.e. solution–mediated is claimed to be responsible for enhancing the formation of  $\text{NaO}_2$  cubes through all the porous cathode thickness and surface.

It has been demonstrated that at low current rates the cathode surface is more homogeneously covered by products, while increasing the current density the distribution becomes inhomogeneous. Surprisingly it is shown that at high rates the majority of the products deposit on the Oxygen reservoir side, i.e. the farther surface from the anode, instead that on the separator side, which should be the common assumption from  $\text{Li} - \text{O}_2$  systems.

Ortiz–Vitoriano et al., besides confirming  $\text{NaO}_2$  as the sole discharge product for Sodium–Oxygen systems (no formation of  $\text{Na}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$  under 6000 ppm of water added to the electrolyte) also performed a study on rate dependency of this product. [25] They confirmed with XRD and Raman spectroscopy that just  $\text{NaO}_2$  was present on their carbon nano–tubes electrodes for all the different current rates applied (i.e. 10, 100, and 1000  $\text{mA g}_c^{-1}$ ), despite the decreasing trend in the discharge potential plateau from 2.2 V at 10  $\text{mA g}_c^{-1}$  to 1.2 V at 1000  $\text{mA g}_c^{-1}$ .

When the current density was 10  $\text{mA g}_c^{-1}$ ,  $\text{NaO}_2$  cubes of less than  $\sim 500$  nm partially covered the top surface of the cathode (i.e. the one facing the oxygen reservoir), smaller cubes of  $\sim 50$  nm were shown by SEM images in the interior of the electrode and again bigger products at the separator/electrode interface ( $\sim 400$  nm). On the other hand, when the current

density was  $1000 \text{ mAg}_c^{-1}$   $\text{NaO}_2$  cubes on both surfaces were one order of magnitude larger ( $\sim 2 - 10 \text{ }\mu\text{m}$  on the top-surface and  $\sim 1.5 - 2.5 \text{ }\mu\text{m}$  on the separator/electrode interface), but within the cathode practically no products were seen. [25]

Janek et al. performed a similar study one year later and the results are from one side confirming the distribution of the products showed in the previous paper, yet from the other side they reported an opposite trend for the size dependency on rates.

They proved that the discharge product, i.e.  $\text{NaO}_2$ , is present predominantly on top of all the cathodes (facing the Oxygen reservoir). Moreover the distribution is clearly more homogenous for lower current ( $100 \text{ }\mu\text{A} \cdot \text{cm}^{-2}$ ), while the higher rates tested showed a gradual increase in product deposition toward the top surface ( $200$  and  $300 \text{ }\mu\text{A} \cdot \text{cm}^{-2}$ ). [32]

The point which does not agree with the previous paper is the particle size dependency. Janek et al. showed bigger particle size with lower current rate instead of with higher like it was previously reported. The size decreased quite linearly from  $30 \text{ }\mu\text{m}$  (maximal edge length) at  $50 \text{ }\mu\text{A} \cdot \text{cm}^{-2}$  to less than  $5 \text{ }\mu\text{m}$  at  $600 \text{ }\mu\text{A} \cdot \text{cm}^{-2}$ .

Additionally they proposed that the higher product density on the top surface could be "due to limited solubility and low diffusivity of  $\text{O}_2$  in the electrolyte" (they used diglyme). [32]

In summary, it has been proved that lower current rates lead to more homogeneous utilization of the porous cathode, yet it is not clear the dependency of particle size and farther how the current can affect the morphology and deposition process of  $\text{NaO}_2$ . A deeper research on this topic could be fundamental to better understand the mechanism going on the  $\text{Na} - \text{O}_2$  system. In fact two papers are not enough to establish a trend, since many factors could have

played a role in the final output, such as cathode, electrolyte, salt, and/or system used.

## CHAPTER 4

### EXPERIMENTAL SET-UP

The purpose of this chapter is to show and explain all the work behind the final results. As already seen during Paragraph 2.2.1, the main components of a battery are: anode, electrolyte, cathode, and catalyst. Thus, these will be the main characters of the following pages, with a final look at the assembly and the experiments performed to test the cells.

#### 4.1 Anode

Sodium is a soft and silvery-white alkali metal and it is highly reactive. The production of pure Sodium is limited to specialized applications and, to avoid its reaction with the environment, it is usually stored and transported immersed in mineral oil or inert gases (normally Argon). Thus, the normal product commercially available are chunks of Sodium of cubical or cylindrical shape.

In order to use it as anode for a battery, a disk  $\sim 1$  cm of diameter and  $\leq 1$  mm thick should be produced. Moreover it obviously need to have surfaces as smooth and shining as possible, avoiding contaminations of all kinds.

The process is made up of three points: 1. removing the contaminated surfaces from the chunk, 2. create a plate of the right thickness ( $\leq 1$  mm), and 3. cut disks with diameters of  $\sim 1$  cm. It should be clear that all these three tasks need to be performed in a controlled environment,

i.e. in a glove-box filled with Argon.

Since Sodium is malleable and its melting point is just at  $98^{\circ}\text{C}$ , two methods have been proposed for the completion of task 2:

- Melting and solidification process;
- Cold pressing.

Task 1 is easy to make, you just need a cutter and a clean surface inside the glove-box to work on. Then we switch to task 2. The first raised process consists in melting Sodium inside a stainless steel pot, then pour it inside an unreactive container, such as polypropylene, press it, and leave it solidifies. It is feasible, but it requires quite a lot of skill, since the whole process must be done inside a glove-box, where the movements are limited. Furthermore a glove-box is usually full of flammable stuff, so the safety of this proposal is at least questionable. In fact it is not a case that everybody prefers the second method.

Cold pressing could be performed quite easily rolling press the pure Sodium chunk previously prepared. The only issue is that Sodium is sticky and tend to glue on all kind of metals, thus a suggested solution is to put the part inside a plastic bag and then proceed with the pressing. This is the method used by practically all the groups working on  $\text{Na} - \text{O}_2$  batteries.

Finally task 3 consists just in cutting the Sodium plate obtained with a circular cutter.

This process (with cold pressing) is the one used for the preparation of all our anodes. In particular the diameters were of 1.15 cm, while the average thickness of 0.5 mm.

Actually it is difficult to be really precise as far as concerns thickness and smoothness of the

surface, since the work is made manually. On the other hand a very low amount of contaminants are present, so the purity of the anode, which is the main point, is preserved.

## 4.2 Separator and Electrolyte

The separator avoids direct contact between anode and cathode, which would result in short circuit, and it should avoid the passage of contaminants (i.e. all the species which are not  $\text{Na}^+$ ) toward the anode.

Two kinds of separator are commonly used: the membrane and the glass fiber. They both could be purchased with different thicknesses and porous sizes.

For our experiments we initially used the glass fiber (Whatman GF/C: 24 mm diameter, 0.26 mm thickness, and  $1.2\ \mu\text{m}$  average pore size), but then we moved to the membrane (Celgard 3501:  $25\ \mu\text{m}$  thickness, and  $0.064\ \mu\text{m}$  average pore size) since we saw a better performance.

The electrolyte is the carrier used by ions to move from anode to cathode and viceversa. It closes the internal electrical circuit of the cell.

Many different electrolytes have been used for the Sodium–Oxygen system, all belonging to the family of non-aqueous electrolyte and, specifically, mostly ether–based (glyme–ether or glycol–ether). Here below I report the most used:

- DME, Dimethoxyethane;
- DGME, Diethylene glycol monoethyl ether;
- DEGDME, Diethylene glycol dimethyl ether;

- TEGDME, Tetraethylene glycol dimethyl ether;
- DMSO, Dimethyl Sulfoxide;
- IL, Ionic liquid, specifically the EMIM – BF<sub>4</sub> (1-Ethyl-3-methylimidazolium tetrafluoroborate).

Within the electrolyte a small amount of salt (obviously containing ions of the metal used as anode, i.e. Sodium) is dissolved, to enhance the mobility properties of the ions and to ensure that the electrolyte is saturated with Na<sup>+</sup>.

The principal salts used in literature are:

- CF<sub>3</sub>SO<sub>3</sub>Na, Sodium trifluoromethanesulfonate or Sodium triflate;
- C<sub>2</sub>F<sub>6</sub>NNaO<sub>4</sub>S<sub>2</sub>, Sodium trifluoromethanesulfonimide or Na-TFSI;
- NaClO<sub>4</sub>, Sodium perchlorate.

The preparation of the electrolyte (here considered as the solvent plus the salt) must happen inside the glove box, since as Sodium metal, also its salts are highly reactive with ambient air. The concentration of the salts is expressed as molarity (mol/l) and here it is reported the simple equation used to compute the right amount for each possible combination.

$$Salt[g] = Volume[l] \cdot Concentration[mol/l] \cdot MolecularWeight_{salt}[g/mol] \quad (4.1)$$

Once calculated the right amount of salt needed for the concentration choosen, it is just a matter of putting it inside a test tube with the help of a precision scale. Then the volume of

solvent decided is added through the use of a pipette.

We performed a systematic study on electrolytes, salts and different concentrations, thus many combinations were prepared. Quite all the systems studied contained an amount of EMIM – BF<sub>4</sub>, because this ionic liquid has a co-catalyst role in cooperation with the catalyst coated on our porous cathode, as we will see in details during next paragraph.

### 4.3 Cathode and Catalyst

The cathode main task is to accommodate the reaction. The most used supporting material is Gas Diffusion Layer (GDL). It is a spongelike material constituted by a packed cluster of carbon fibers, whose purpose is to provide an electrically conductive route for current. This structure is quite always used in collaboration with a catalyst, which main task is to create nice spots for the reaction to start, i.e. the so called active sites.

Different GDL have been used or other similar structures with the same duty, but the most important role is played by catalysts. Some groups usually buy carbon cathode already coated with some catalyst, others prepare themselves their catalysts and personally perform the coating on a "virgin" GDL commercially available.

Our laboratory belongs to the second group, so we just purchase a GDL (from FuelCellsEtc, Sigracet 25 BC: 235  $\mu\text{m}$  thickness, 86 g/m<sup>2</sup> areal weight, and 80 % porosity) and then we apply the coating of our catalyst, i.e. MoS<sub>2</sub> nanoflakes, by hand.

The preparation starts from the MoS<sub>2</sub> nanoflakes using a modified liquid exfoliation method.

[6] First we wash one glass baker (100 ml volume) and one stainless steel spatula with Aceton, then with Isopropyl Alcohol (IPA) and in the end with Deionized water (DI water). Now these two pieces are dried using Nitrogen ( $N_2$ ). It is fundamental that absolutely no water is present after the drying, so it must be done carefully.

The following step is to use the spatula to take 0.31 g of bulk Molybdenum disulfide (commercially available) and put it inside the baker. Then the baker is filled up to 60 ml with IPA, making sure that the  $MoS_2$  has been completely dissolved.

The prepared solution must be covered with parafilm to avoid squirts during the next phase and, in general, contaminations. At this point the baker is ready to be used for the sonication. The sonicator produce high-frequency mechanical waves, which perform the breaking of the weak Van der Waals bonds between the covalent bonded layers of  $MoS_2$ , thus forming the previously cited nanoflakes. The batch undergoes sonication for 30 hours using a sonication probe (Vibra Cell Sonics 130W). [6]

After that the solution needs to be centrifugated, to separate the bigger residuals (solid phase) from the actual nanoflakes suspended in the IPA (liquid phase). The centrifugation goes on for 1 hour at 2000 rpm. Then we just need to take the solution out from the centrifuge and we obtain a solution of  $MoS_2$  nanoflakes (average flakes size of 135 nm) in IPA ready for the coating.

The second stage consists in preparing the GDL and coating the solution obtained. First we cut some GDL (we usually do a square cut 5x5 cm), then we weight it in order to have a control on the amount of catalyst we are depositing in our cathode. Our optimized density

of catalyst is  $0.0001 \text{ g/cm}^2$ , thus in a 5 by 5 cm square the total weight of catalyst should be 0.0025 g.

Hence we start the coating, which consists in gently spreading the solution on the GDL (on the side of higher porosity, i.e. lower pores) with a brush, previously washed in IPA. After each surface coat the solution is left under a lamp to let it dries. This treatment is repeated "n" times, till we reach the final weight computed before, being aware of the slowness of the complete evaporation process (i.e. leaving the GDL to dry for some hours after a good number of wipes).

Finally we obtain a homogeneously coated square cathode, so we need just to cut it with the circular cutter to get the ready to use cathode: 1.15 cm diameter and  $235 \text{ }\mu\text{m}$  thick. It is good to notice that the final surface of the cathode is  $\simeq 1.04 \text{ cm}^2$ , thus the quantity of catalyst per cell will be just 0.0001 g.

#### **4.3.1 The Catalytic Activity of $\text{MoS}_2$ and EMIM – $\text{BF}_4$**

Last year our group, in collaboration with other researchers, demonstrated the optimum catalytic activity of the team  $\text{MoS}_2/\text{IL}$  as far as concerns ORR and OER.

One of the main challenge in the battery field is to find a combination of cathode and electrolyte which is "efficient, stable, and cost-effective". [6]  $\text{MoS}_2$  and IL have proved to be one possible candidate, showing incredibly high performance when used in a  $\text{Li} - \text{O}_2$  system.

The formation of  $\text{Li}_2\text{O}_2$  (i.e. the main product in  $\text{Li} - \text{O}_2$  batteries) has been debated for a long time, yet it seems that lately the solution-mediated process has gained more consent than

the direct growth on the cathode.

The through-solution mechanism starts with the formation of  $\text{O}_2^-$ , which then dissolves in the electrolyte. Here oxygen ions react with  $\text{Li}^+$  forming  $\text{LiO}_2$  (Lithium superoxide). Finally the superoxides likely form dimers  $(\text{LiO}_2)_2$ , that can disproportionate to form  $\text{Li}_2\text{O}_2$ .

At this point, since  $\text{Li}_2\text{O}_2$  is not highly soluble, it starts depositing by nucleation and growth on the electrode. [6]

Now let's analyze how IL interacts with  $\text{MoS}_2$  and why it works better than other electrolytes. When a normal electrolyte is used, in this case DMSO, its molecules are pretty neutral and bind only weakly to the Mo edges. Thus  $\text{O}_2$  molecules easily replace DMSO or bind directly on the free Mo edges. After that they rapidly dissociate to two-bounds O atoms on the Mo edge. In some cases this two O atoms can rearrange to form an active site, in which  $\text{O}_2$  can be reduced to  $\text{O}_2^-$ . However thermodynamics drives the reaction toward a full oxidation of the Mo edges, which results in a complete poisoning of the catalyst.

Things change when DMSO is replaced by IL, in particular  $\text{EMIM} - \text{BF}_4$ . IL cations are strongly attracted by cathodes, while IL anions by anodes. Calculations show that  $\text{EMIM}^+$  are very likely to bind to the Mo nanoflakes. [6] Given the size of those molecules, they probably arrange on the cathode leaving one Mo atom free between one another. These free Mo atoms are active sites for ORR. Thus the strong interaction between  $\text{MoS}_2$  nanoflakes and  $\text{EMIM}^+$  prevents the dissociation of  $\text{O}_2$  and, in turn, the complete oxidation of the catalyst.

Therefore  $\text{O}_2^-$  ions are formed and rapidly desorbed into the IL due to the strong solvation effect, populating the electrolyte. [6] At this point they need just to encounter some  $\text{Li}^+$  to

start the reactions that will finally lead to the formation of  $\text{Li}_2\text{O}_2$ .

In summary, has been demonstrated that  $\text{MoS}_2$ , when used in combination with IL, is an efficient and low-cost catalyst for the Oxygen in battery applications.

#### 4.4 Assembling

Once all the components are prepared, what remains is just to assemble the cell. We use a Swagelok kind cell with pressure gauge and we assemble it inside a glove box.

The artificial environment inside the working station is Argon filled, with some little amounts of impurities ( $\leq 0.01$  ppm of water and  $\leq 1.0$  ppm of oxygen) and pressure around 1 atm. First of all the instruments are washed with a solvent, such as DMC (Dimethyl Carbonate), to avoid contaminations, then the assembly could start. Here below I report the algorithm followed for the preparation (keep an eye on Figure 7):

1. Lay down the spacer ring made of stainless steel;
2. Place the stainless steel current collector over the ring;
3. Place the sodium anode on top of the current collector;
4. Deposit the separator on the anode;
5. Put a few droplets (2 or 3 depending on the kind of separator) of electrolyte on the separator using a pipette;
6. Gently lay down the cathode (coated surface facing the separator);
7. Close the cell precisely.

It is important that all the components are as much as possible concentric, to perform a uniform contact between all of them. Moreover not too much pressure should be applied in sealing the cell with the four adjustable screws, otherwise short-circuit is likely to happen.

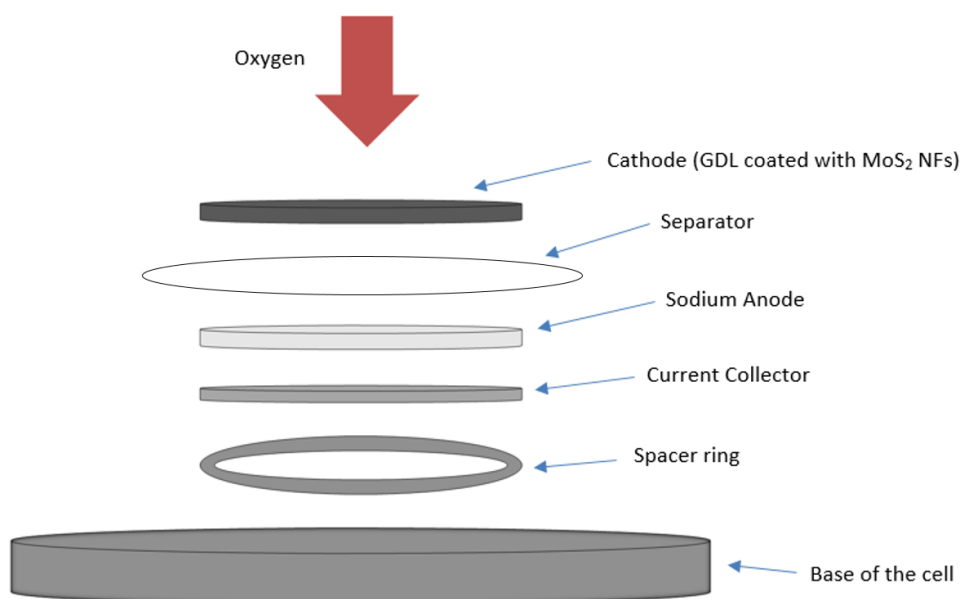


Figure 7: Schematic representation of the assembly of a Swagelok cell.

Once the assembly is completed, to double-check if the work has been performed well, it is usually measured the open circuit potential of the cell, which should be similar to the theoretical (i.e. 2.27 V for Sodium).

At this point we just have to pump Oxygen in the cell through the inlet valve. In order to be sure that the system has time to reach an equilibrium, Oxygen is poured with both inlet and outlet valves open for at least 5 minutes. It is important to let the oxygen flow some seconds

before purging it inside the cell, to fill the connecting tube with  $O_2$  and so to limit contaminants from ambient air. After that, with the outlet valve closed, the pressure is increased till the desired point (for our experiments we keep 0.08 MPa as vacuum pressure gauge) and finally also the inlet valve is closed.

Now the cell is ready to be tested.

#### 4.5 Experiments

The main device used to test electrochemical cells is the potentiostat.

It is a control and measuring instrument which is able to keep a constant current, whatever changes in the load. It is able to maintain a wide range of current rates (from picoamperes to amperes) of both polarities, adjusting the output potential when an alteration in resistance (of the cell) occurs.

We employ a battery analyzer (BST8-MA: 30 W power, 0.02–10 mA current range, 0.5–5 V voltage range, and 1–900 s time interval).

There are two principal experiments to test the discharge and charge ability of an electrochemical cell:

1. Deep discharge and charge;
2. Shallow cycling.

Deep discharge and charge aims to test the maximum reversible capacity of the system, i.e. the maximum amount of energy that can be stored in the cell reversibly. Once set the current rate,

the cell is discharged till the point of cut-off potential.

This cut-off value depends on the system and it is generally a value under which the potential would be so low that the efficiency of the system would be too small (for Sodium is normally set between 1.2 and 1.8 V). However is difficult to find an accepted definition of efficiency, thus those cut-off values are just taken from literature.

When the discharge potential reaches the lower cut-off, the charge is started and it continues till the higher cut-off. This procedure could be repeated and many cycles could be performed. The important result in this kind of test is the reversible capacity. It is usual that the discharge shows higher capacity than the charge, thus the reversible capacity is intended to be the one during charge.

The capacity is easily computed with Equation 4.2.

$$Capacity[mAh] = Current\ rate[mA] \cdot Time[h] \quad (4.2)$$

The second experiment differs from the first one because here the capacity is previously set, limiting the discharge and charge time. The point of shallow cycling is to show a reversible system able to work with similar performance for many cycles. The current rates most used are 0.05 and 0.02 mA, yet also other values are sometimes explored (such as 0.01, 0.1, 0.2, 0.5, or 1.0 mA). One big problem of electrochemical field is that current rates and capacity are always weighted on the surface of cathode or on the amount of catalyst used, making practically impossible to compare results if some data are hidden.

We usually employ a current rate of 0.05 mA for 1 hour discharge and 1 hour charge, which means 0.05 mAh, that, considering 0.0001 g of catalyst per cathode, becomes 500 mAh/g.

## CHAPTER 5

### RESULTS

#### 5.1 Looking for the Best Combination of Electrolyte and Salt

Every new research path requires a beginning, and the first decisions are often the more challenging. For Sodium–Oxygen, at the time we started this project, there was the presupposition that, since Na is an alkali as Li, it should have very similar electrochemical properties to Lithium. Therefore the wiser opinion seemed to start from electrolyte and salts already and commonly used for Li – O<sub>2</sub> batteries.

In our laboratory, the component which mainly made the difference from other groups is the catalyst. As we previously saw (Paragraph 4.3.1), MoS<sub>2</sub> nanoflakes, coated on the GDL, work in combination with the ionic liquid EMIM – BF<sub>4</sub> to enhance ORR and OER. Thus the presence of EMIM – BF<sub>4</sub> in the electrolyte is vital to make the catalytic system work properly.

The last consideration is that in complicated systems like those batteries there are many factors that could affect the performance, so it is important to choose one or two parameters and perform a study on those, trying to keep all the other variables untouched, to avoid contamination of the results.

The first study carried out is about electrolytes and salts and the target is to explore a wide range of combinations in order to find the one which is working to the best with our particular

system.

All the other affecting factor were kept as much as possible constant:

- anodes were prepared inside the glove box and replaced as soon as they started to oxidize, changing colour;
- carbon cathodes coated with  $\text{MoS}_2$  nanoflakes have always been prepared following carefully the procedure previously reported;
- the membrane (Celgard 3501: 25  $\mu\text{m}$  thickness, and 0.064  $\mu\text{m}$  average pore size) was used as separator for all the results showed;
- the assembly was always carried out by the same person with a standard procedure;
- the experiments performed were shallow cycling with capacity of 500 mAh/g, obtained running the cell for 1 hour discharge and 1 hour charge at the current rate of 0.05 mA.

The first step was to demonstrate the reversibility of Sodium–Oxygen using as electrolyte the ionic liquid  $\text{EMIM} - \text{BF}_4$ . In doing so we prepared a solution where 0.5 M of  $\text{Na-TFSI}$  were dissolved in IL. We employed as salt  $\text{Na-TFSI}$  because the lithium counterpart  $\text{Li-TFSI}$  showed good stability and it is widely used in  $\text{Li} - \text{O}_2$  batteries. We tried to run one cell and in Figure 8 the resulting first cycle is shown.

It is clear that the system is reversible with a capacity of 500 mAh/g. However, while the discharge overpotential is of about 0.2 V, the charge overpotential is  $\sim 2.0$  V, resulting in a potential gap of more than 2 V. The system is not working properly, since a one-electron transfer should lead to very low polarization gap, yet we are not going to use the  $\text{EMIM} - \text{BF}_4$  as main electrolyte, the point was just to demonstrate the reversibility of the system.

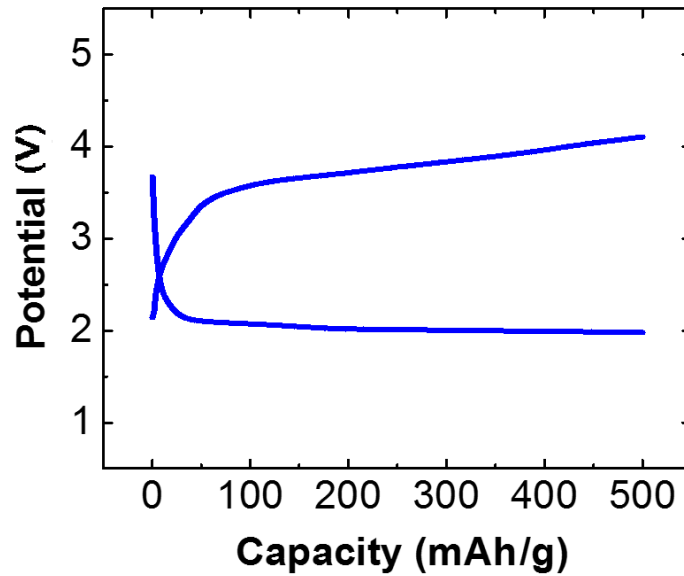


Figure 8: First shallow cycle of a Na – O<sub>2</sub> Swagelok cell with 0.5 M of Na-TFSI dissolved in EMIM – BF<sub>4</sub> as electrolyte.

The following step consisted in preparing an electrolyte similar to the one used from our group in Li – O<sub>2</sub> batteries with amazing performance (IL and DMSO 1/3 plus 0.5 M of Li-TFSI). Thus the solution was made by 75 % of DMSO and 25 % of IL, plus 0.5 M of Na-TFSI. This was the actual first system tested (see Figure 9).

As we can see the system started with a quite low polarization gap of  $\sim 0.75$  V, but it rapidly increased up to  $\sim 1.5$  V after just 5 cycles. Then the cell performance started to get always worse (after 8 cycles the gap is more than 2.0 V), probably due to accumulation of side products, till it failed.

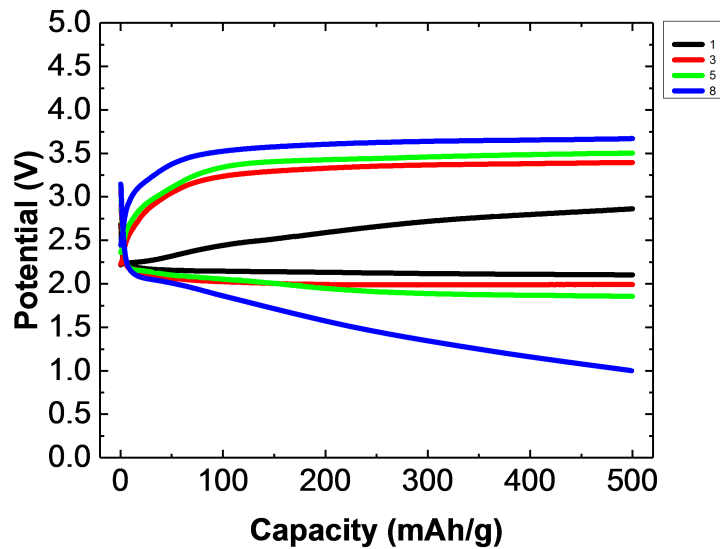


Figure 9: Shallow cycling of a Na – O<sub>2</sub> cell with 0.5 M of Na–TFSI dissolved in EMIM – BF<sub>4</sub> and DMSO (in relation 1/3) as electrolyte.

We continued our study, testing the performance of another salt, the most reported in literature for Na – O<sub>2</sub> batteries, the Na–triflate. A new cell with 0.5 M of Na–triflate dissolved in a solution made by 75% of DMSO and 25% of IL as electrolyte was assembled. The performance obtained is reported in Figure 10.

The polarization gap is incredibly low during the first cycles, starting from  $\sim 0.1$  V in the first one, to  $\sim 0.55$  V after 5 cycles. However again we see a sharp increase in the gap approaching the tenth cycle ( $\sim 1.3$  V) and the consequent failure of the cell.

We deduced that the Na–triflate is working better than the Na–TFSI in this system.

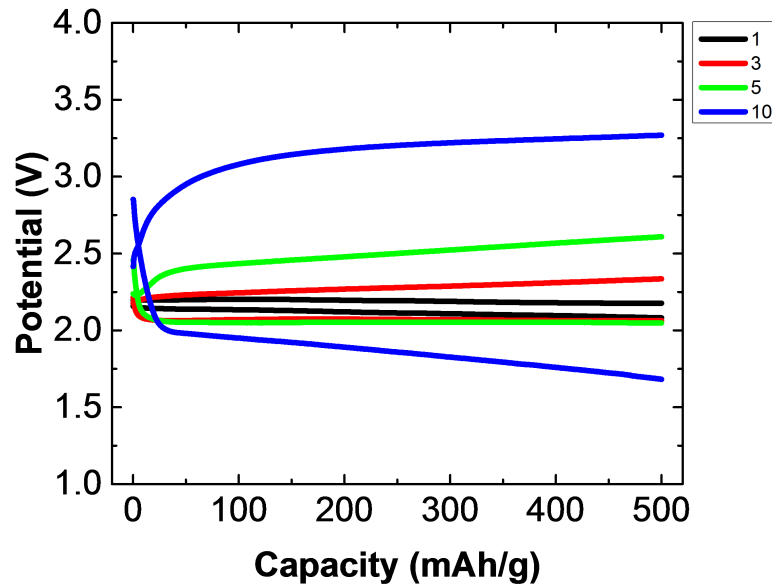


Figure 10: Shallow cycling of a Na – O<sub>2</sub> cell with 0.5 M of Na-triflate dissolved in EMIM – BF<sub>4</sub> and DMSO (in relation 1/3) as electrolyte.

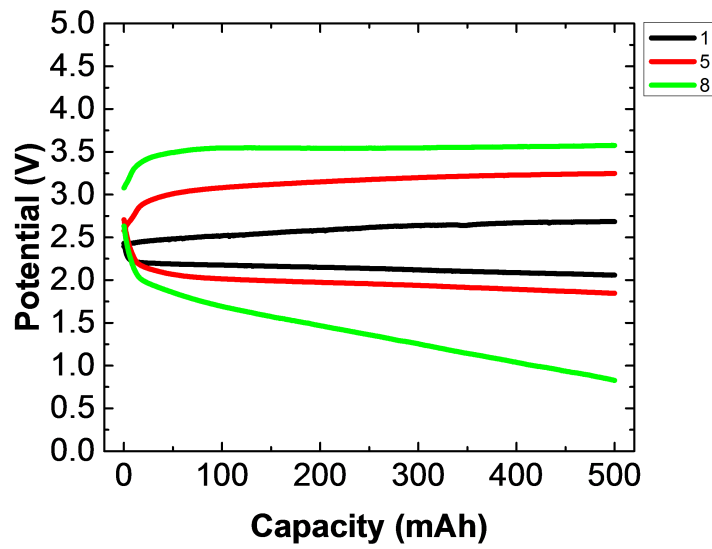
After that we explored also a different salt (NaClO<sub>4</sub>), since it showed good performance with another electrolyte tested (TEGDME). The NaClO<sub>4</sub> in TEGDME works better with concentration of IL lower than 25% as we will see later, thus we prepared two different electrolytes:

**a** 0.5 M of NaClO<sub>4</sub> in 90% of DMSO and 10% of IL (Figure 11(a));

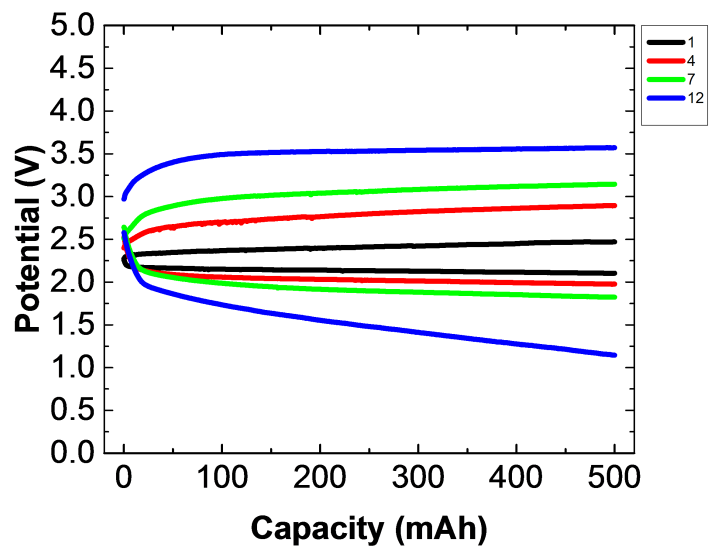
**b** 0.5 M of Na-triflate in 90% of DMSO and 10% of IL (Figure 11(b)).

Those two experiments let us understand two things. First the Na-triflate works better with DMSO than the NaClO<sub>4</sub>, in fact the performance of both polarization gap and cycle life are better for the system with the Na-triflate. Second that a lower concentration of IL results in an increased cycle life, but, on the other hand, it reduces the efficiency of the cell, increasing

the polarization gap.



(a)



(b)

Figure 11: Shallow cycling of two Na – O<sub>2</sub> cells with EMIM – BF<sub>4</sub> and DMSO (in relation 1/9) as electrolyte, a) 0.5 M of NaClO<sub>4</sub>, b) 0.5 M of Na-triflate.

At this point we performed different studies keeping the concentration to 0.5 M.

We tried other 3 electrolytes: DME, DGME, and TEGDME. With DME our system was very unstable and we could not even reach 5 cycles and with DGME the performance were worse than with DMSO, thus there is no meaning in reporting those results.

On the other hand we found a high cyclability employing TEGDME as electrolyte. First we tested a cell with the previous best combination of concentration of solvents and salt, so a system in which 0.5 M of Na-triflate was dissolved in 75 % of TEGDME and 25 % of IL (see Figure 12).

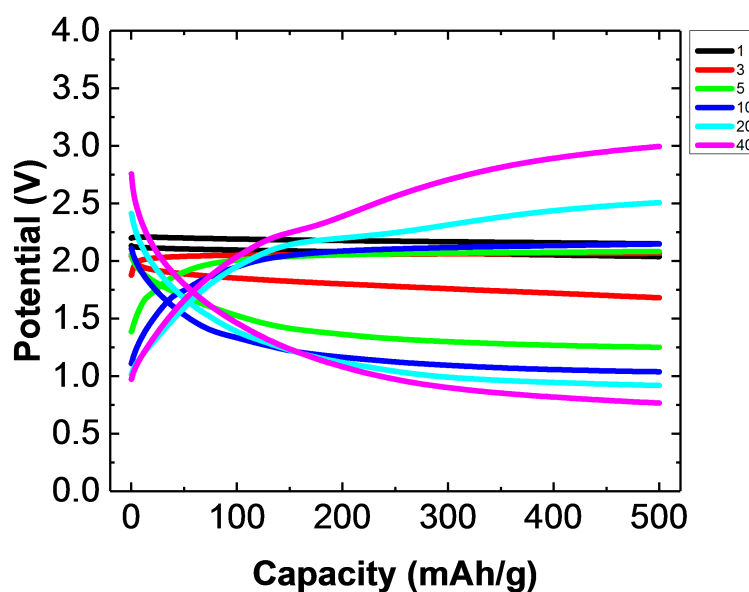


Figure 12: Shallow cycling of a Na – O<sub>2</sub> cell with 0.5 M of Na-triflate dissolved in EMIM – BF<sub>4</sub> and TEGDME (in relation 1/3) as electrolyte.

Looking Figure 12 we notice that the potential gap is similar to the one in Figure 10, where the DMSO was used; yet a cyclability four times higher is reported changing the electrolyte. It is also worth saying that the increase in potential gap occurred faster with TEGDME than with DMSO.

We had another proof of the high cyclability obtainable using TEGDME, testing as electrolyte a solution of 0.5 M of  $\text{NaClO}_4$  in TEGDME.

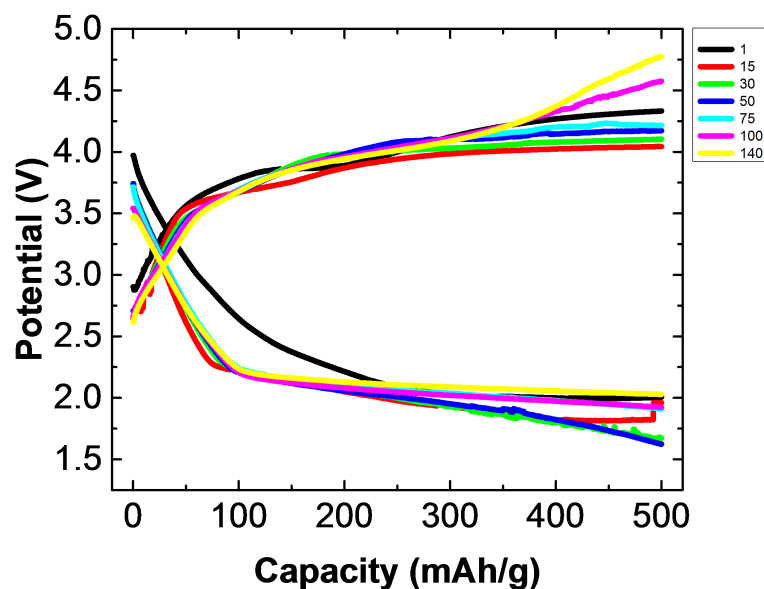


Figure 13: Shallow cycling of a  $\text{Na} - \text{O}_2$  cell with 0.5 M of  $\text{NaClO}_4$  dissolved in TEGDME as electrolyte.

The result of Figure 13 show a very good stability of the system, which reached 75 cycles with a polarization gap of  $\sim 2.0$  V, and then it failed after 140 cycles, reaching a gap of  $\sim 3.0$

V. We concluded that this combination of salt and electrolyte was the best one for our system and we started to think about how to reduce the polarization gap and make this Na – O<sub>2</sub> cell work properly, i.e. with a low polarization gap. In doing so we performed a study on the concentration of ionic liquid added to the main electrolyte.

We started from the concentration usually used in the Li – O<sub>2</sub> system, i.e. 75 % of TEGDME and 25 % of IL.

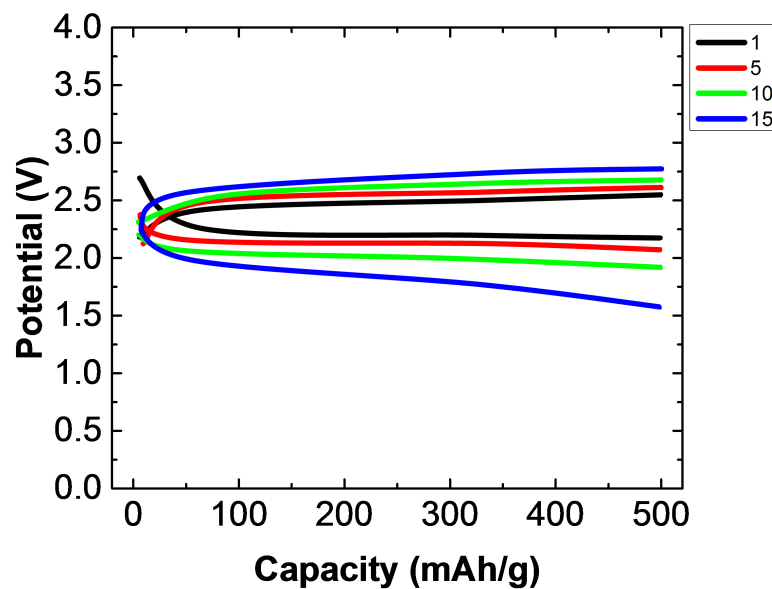
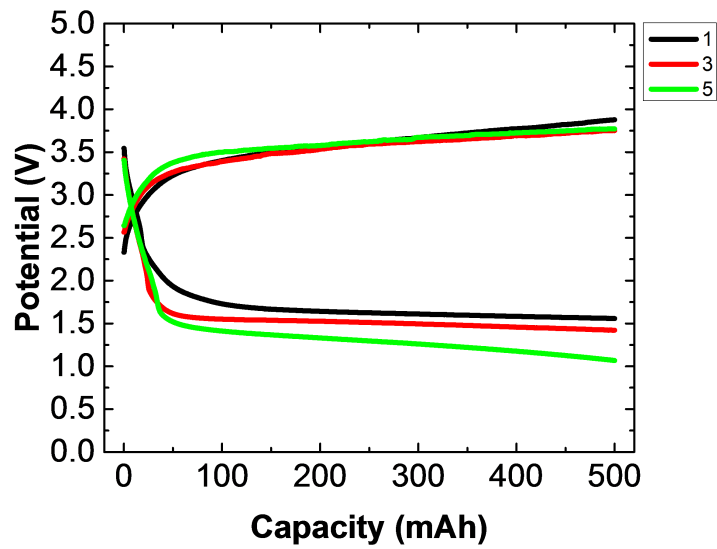


Figure 14: Shallow cycling of a Na – O<sub>2</sub> cell with 0.5 M of NaClO<sub>4</sub> dissolved in 75 % of TEGDME and 25 % of IL as electrolyte.

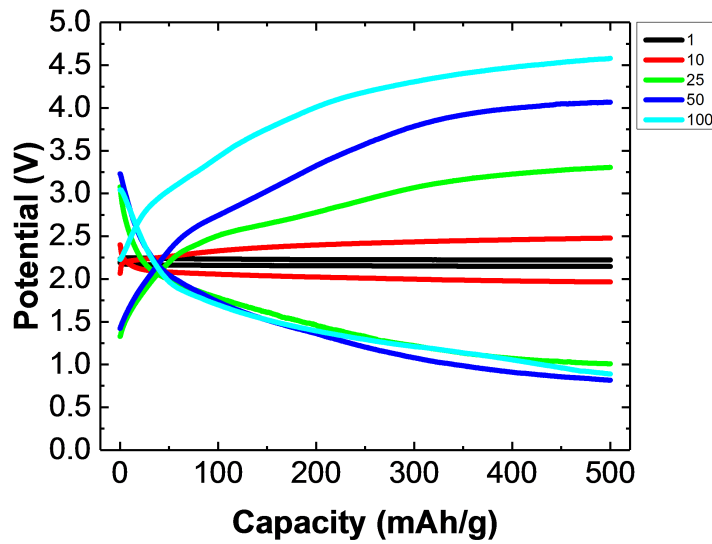
After that we explored higher and lower concentration.

First we tested a cell with 0.5 M of NaClO<sub>4</sub> were dissolved in 50 % of TEGDME and 50 % of

IL (Figure 15(a)). Then we moved to lower concentration and we employed as electrolyte 0.5 M of  $\text{NaClO}_4$  were dissolved in 90 % of TEGDME and 10 % of IL (Figure 15(b)).



(a)



(b)

Figure 15: Shallow cycling of two Na –  $\text{O}_2$  cells with 0.5 M of  $\text{NaClO}_4$  dissolved in EMIM –  $\text{BF}_4$  and TEGDME as electrolyte, a) 50 % of TEGDME and 50 % of IL, b) 90 % of TEGDME and 10 % of IL.

It is clear from the results that decreasing the ionic liquid concentration in the electrolyte the performance are enhanced, at least till reaching the realation main-solvent/IL of 1/9. In fact when the ratio was 50/50 (Figure 15(a)) the gap was about 3.0 V and the cell did not last more than 5 cycles, while when the proportion was decreased to 25/75 (Figure 14) the efficiency was highly enhanced, with 10 cycles under 1.0 V of potential gap, yet the stability of the system was low and the cell died after just 15 cycles. Then, when the ratio was 10/90 (Figure 15(b)) the system was able to reach more than 100 cycles before having a potential gap of about 3.0 V and it showed also high efficiency till the tenth cycle, with a gap lower than 0.5 V. Ultimately, when no IL was present in the system, no catalytic activity is expected, thus it seems reasonable to have a higher potential gap for the cell shown in Figure 13; yet, on the other hand, it performed more than 140 cycles, demonstrating stability of the electrolyte and a good cyclability. Thus we deduced that the EMIM – BF<sub>4</sub> on one side was improving the efficiency of the system, decreasing the energy required from the reaction to happen, but, on the other side, it was also increasing the side reactions, and in turn the cycle life of the cell. This must be taken into account for further improvement of this system, maybe trying to find another IL which is more stable with sodium.

Finally, to double-check our choice of using NaClO<sub>4</sub> instead of Na-triflate, we tested a cell with 90 % of TEGDME and 10 % of IL as solvent and 0.5 M of Na-triflate as salt. As we can see from Figure 16, the polarization gap increased rapidly and also the stability was low, resulting in the death of the cell after just 15 cycles.

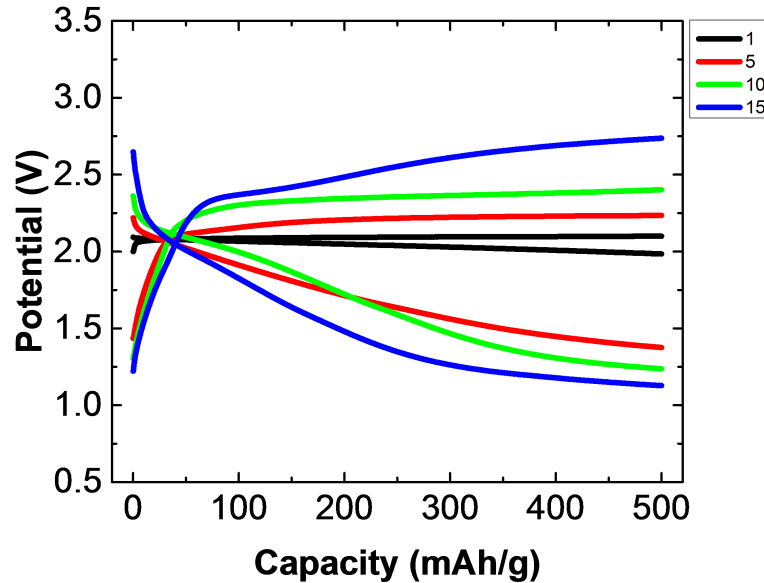


Figure 16: Shallow cycling of a Na – O<sub>2</sub> cell with 0.5 M of Na-triflate dissolved in 90 % of TEGDME and 10 % of IL as electrolyte.

## 5.2 Systematic Study on Current rate and Salt Concentration

After the detailed screening of different electrolytes and salts reported in the previous paragraph, we concluded that the best combination for our specific system is 0.5 M of NaClO<sub>4</sub> dissolved in a solution made by 90 % of TEGDME and by 10 % of IL (Figure 15(b)). The next step done was a systematic study on the influence of salt concentration and current rate on the performance of the battery.

The first concern we had about our system was on the order of magnitude of the dimensions in the game. Our porous cathode contains particles of the nano-scale range (the MoS<sub>2</sub> nanoflakes), while the products formed during discharge are reported to be in the micron-scale (cubic edges

of 5–10  $\mu\text{m}$ ). So how could it be possible that those relatively big  $\text{NaO}_2$  cubes fit comfortably on our coated GDL?

Recently, some groups were claiming that an increase in the current rate would lead to a decrease in the particle size. This studies got us the idea to explore higher current rates in order to improve the exploitation of our cathode.

One important point was to be consistent with results at different currents, so we decided to keep constant the capacity of the system, since it is strictly related to the quantity of products formed. In doing so we decrease the time of cycling, consistently with the Equation 4.2.

The first experiment carried out was with double current and half time than usual, i.e. 0.1 mA for cycles of 30 min discharge and 30 min charge (Figure 17).

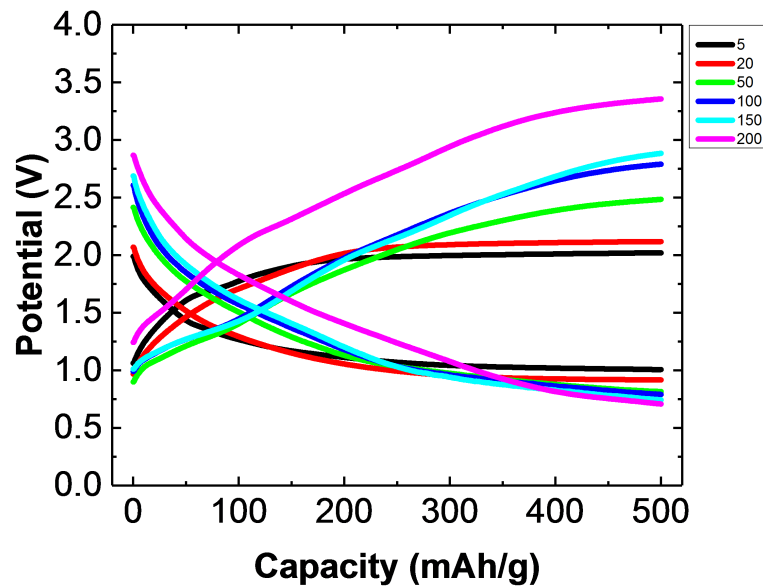


Figure 17: Shallow cycling of a Na –  $\text{O}_2$  cell with 0.5 M of  $\text{NaClO}_4$  dissolved in 90 % of TEGDME and 10 % of IL as electrolyte at 0.1 mA/cm<sup>2</sup>.

We noticed an increase in both cyclability and efficiency in the long run, in fact it took more than 200 cycles to reach a polarization gap of about 3.0 V. We attributed this behavior to the predicted decrease in size of the products, which could facilitate both deposition (due to the increased number of comfortable spots) and dissolution (due to the increase in the total surface of the products). Instead the efficiency of the system in the first cycles is remarkably reduced. The polarization gap reached 0.5 V after 10 cycles when the cell was tested at 0.05 mA, while it was more than 1.0 V after just 5 cycles with a current of 0.1 mA. The more, the average potential between charge and discharge fell from  $\sim 2.3$  V to  $\sim 1.6$  V, resulting in a vertical shift of the cycles of 0.5 V on the Potential vs. Capacity graph.

However it seemed too soon to make conclusion, thus we continued our study, increasing the current up to 0.2 mA (Figure 18).

The result confirmed the trend, showing another increase in both cyclability and efficiency of the cell. As we see, it reached more than 500 cycles with a potential gap of about 2.0 V. This is the highest cyclability ever showed by a Na – O<sub>2</sub>, but it is worth saying that the polarization gap is still too high to be competitive with Lithium system and the more important, the time of cycling is highly reduced respect from common intervals (more or equal to 1 hour).

This interesting result on one side let us confirm our hypothesis that smaller products lead to a facilitation in the process of dissolution. In fact the easier dissolution, i.e. charge, is reflected in the charge overpotential, which increases very smoothly during the cycling, reaching just 0.75 V after 500 cycles.

On the other side, it also confirm the decreasing trend in the average potential which become  $\sim 1.4$  V. This trend is due to the decreasing behavior of the discharge potential, i.e. increase

in discharge overpotential, which could be explained as a raised difficulty in the deposition for the products. Thus high current rates seems to facilitate charge but also to make difficult the discharge.

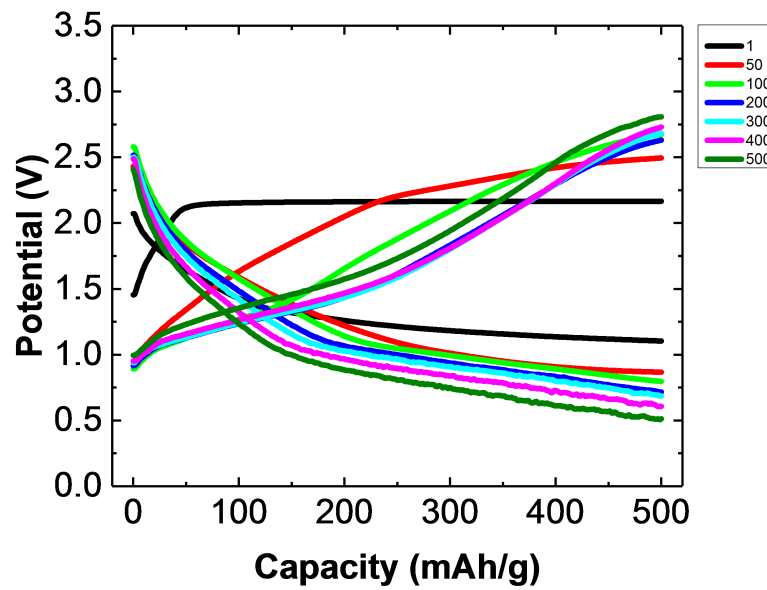
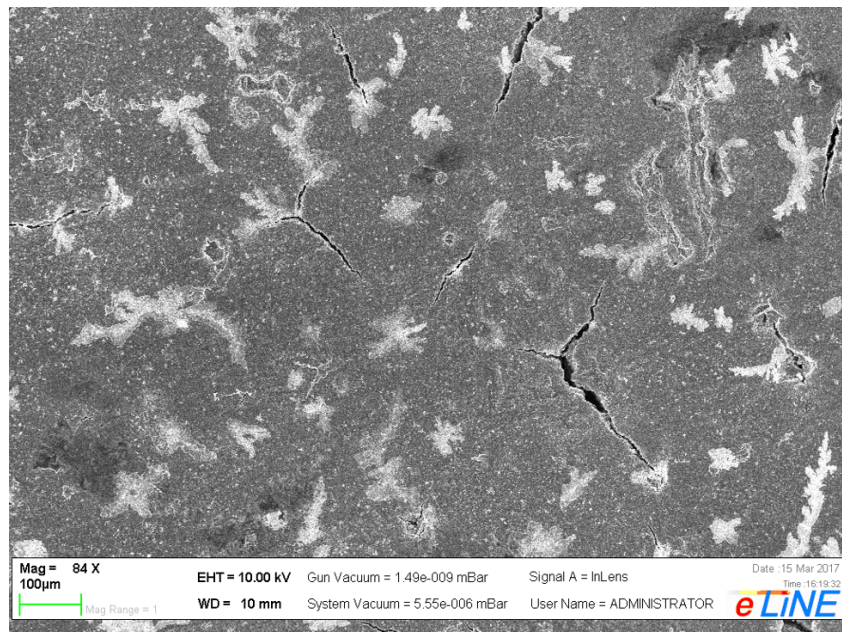


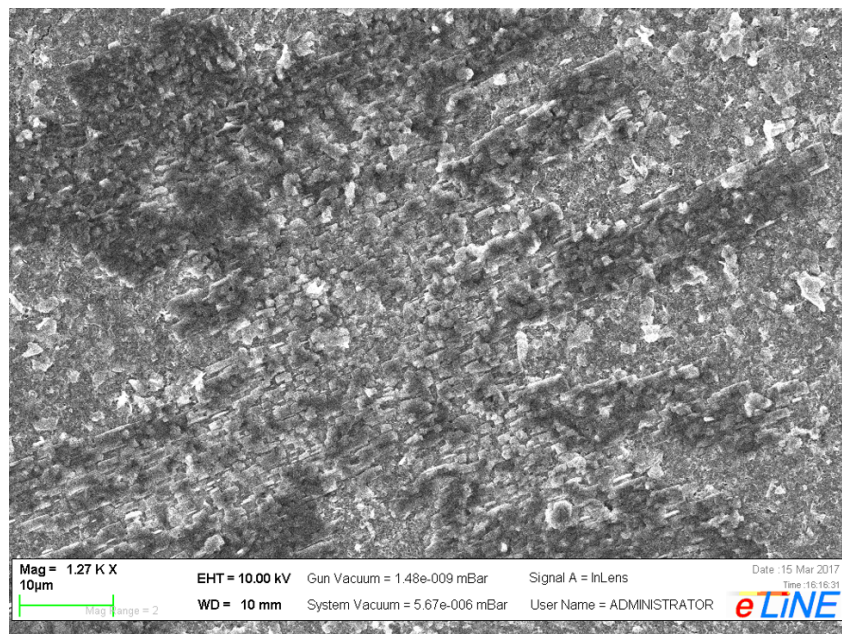
Figure 18: Shallow cycling of a Na – O<sub>2</sub> cell with 0.5 M of NaClO<sub>4</sub> dissolved in 90 % of TEGDME and 10 % of IL as electrolyte at 0.2 mA/cm<sup>2</sup>.

Someone could argue that this system is not working with a one-electron transfer process and that we are producing peroxide instead of superoxide, since the potential gap is quite wide. We also made that hypothesis, so we performed a SEM characterization of the cathode right after the shallow cycling test, to visualize our products.

The obtained pictures are reported in the next pages.

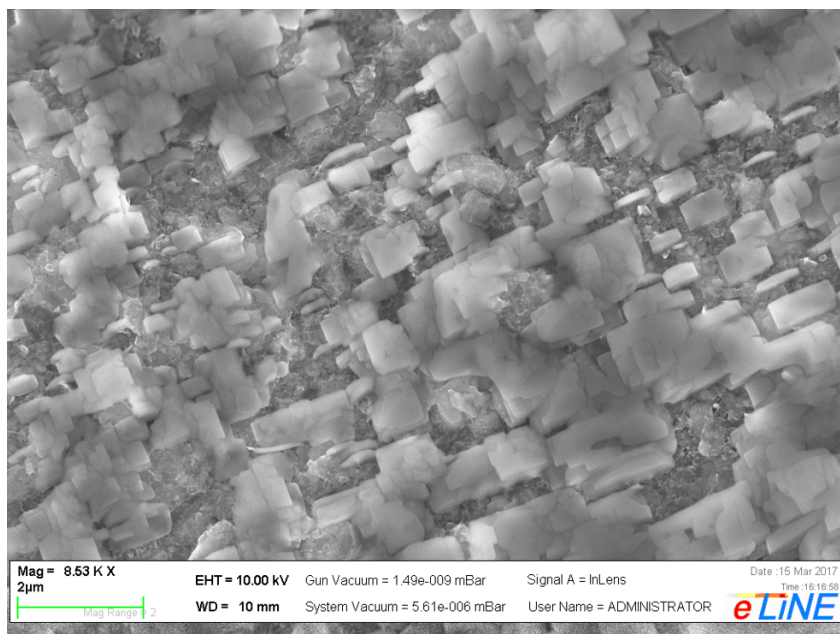


(a)

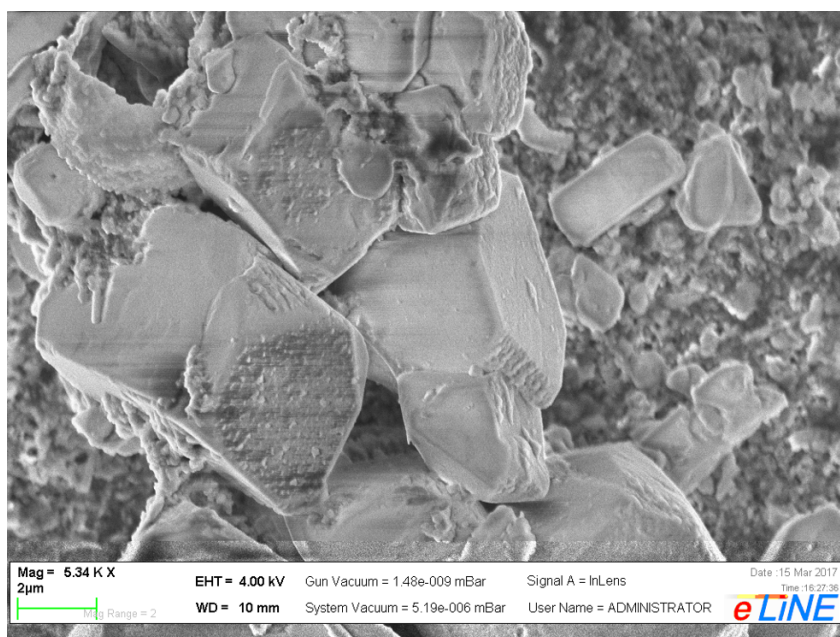


(b)

Figure 19: SEM pictures at low magnification of the  $\text{MoS}_2$  coated surface of the GDL (i.e. the cathode), a) Mag = 84 X, b) Mag = 1.27 K X.



(a)



(b)

Figure 20: SEM pictures at high magnification of the MoS<sub>2</sub> coated surface of the GDL (i.e. the cathode), a) Mag = 8.53 K X, b) Mag = 5.34 K X.

As we clearly see from the high magnification images (Figure 20(a) and Figure 20(b)) the products have the typical cubic shape which belongs to  $\text{NaO}_2$  and not the toroidal and asymmetric appearance of sodium peroxide.

Even if many characterizations are needed to prove the presence of  $\text{NaO}_2$ , the similarity with other reported studies made us speculate that we were actually producing superoxide, so that another factor had to be responsible for the decrease in the discharge plateau experienced at high current rates.

A battery is a very complicated system and many factors contribute to the final outcome, so it is difficult or sometimes impossible to attribute to a particular behavior just one exact reason. However hypothesis could be made, and, taking ideas from literature, we thought to diffusivity and ions mobility as the factors playing the main rules in this system and which are mostly influenced by the increasing in current rate.

As I reported in Chapter 3, many studies have been performed on  $\text{Na} - \text{O}_2$  batteries and many ideas have been explored. The low mobility of Oxygen ions is often claimed as one of the main reasons which lead to the failure of the cell and the solution-mediated process of formation and dissolution of products have not yet been deeply understood. Anyway both scenarios could highly affect the performance of the cell, from the cycle life to the polarization gap. So our assumptions are at least reasonable, yet more experiments and studies need to be executed in order to truly understand the reasons behind this decrease in the discharge plateau.

Returning to our experiments, we continued to increase the current rate, to see if and when

the system would have reached a maximum. Hence we ran a cell at the current rate of 0.3 mA (Figure 21).

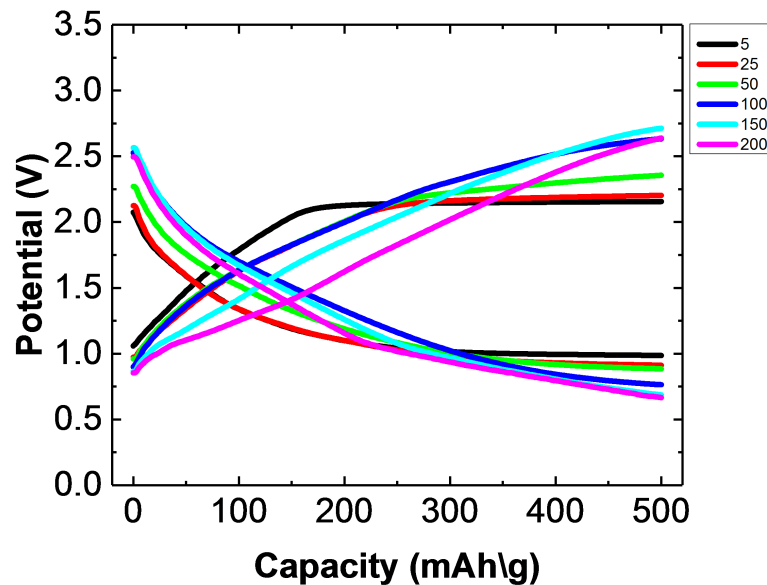


Figure 21: Shallow cycling of a Na – O<sub>2</sub> cell with 0.5 M of NaClO<sub>4</sub> dissolved in 90 % of TEGDME and 10 % of IL as electrolyte at 0.3 mA/cm<sup>2</sup>.

Since it was reported a decrease in product size till an increased current of  $600 \mu\text{A} \cdot \text{cm}^{-2}$  (which corresponds to about 0.6 mA), we were expecting other increases in cyclability and efficiency. [32] Unfortunately the cell acted very similarly to the one tested at 0.2 mA and indeed with a slightly higher polarization gap.

We concluded that the 0.2 mA was already the start of a plateau in the performance dependency on higher current rate, thus, to conclude our study, we moved to lower current rate.

The following experiment was run at a current of 0.025 mA and the results are showed in Figure 22.

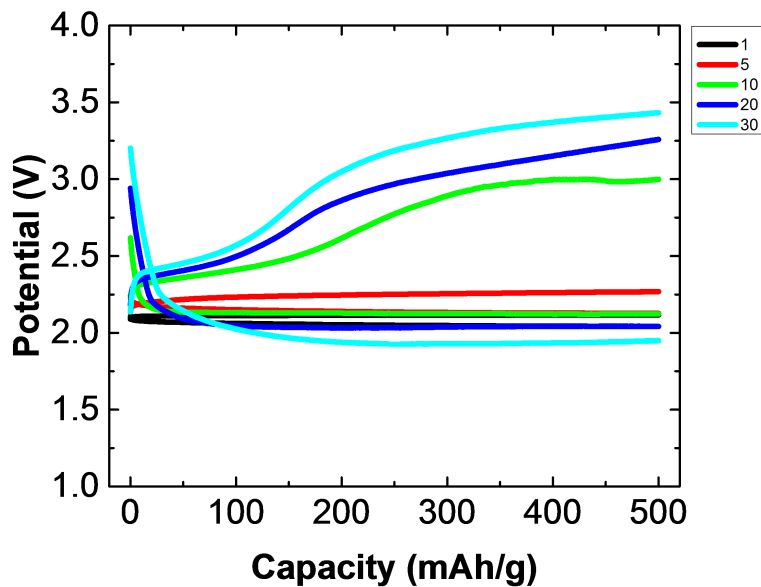


Figure 22: Shallow cycling of a Na – O<sub>2</sub> cell with 0.5 M of NaClO<sub>4</sub> dissolved in 90 % of TEGDME and 10 % of IL as electrolyte at 0.025 mA/cm<sup>2</sup>.

The cell performed the first 5 cycles with an astonishing efficiency, with a potential gap lower than 0.25 V. However, after these, the charge overpotential started to increase rapidly and at the 30<sup>th</sup> cycle the polarization gap was already near 1.5 V.

The reduced current rate seemed to favor the discharge phase, in fact the discharge overpotential is less than 0.2 V after 30 cycles, yet the cyclability is considerably lowered. This could be due to side products formation or, following the previous reasoning, to the difficulty encountered

in dissolving big products formed during a slow discharge which in turn lead to clogging of the porous cathode.

In summary, it seems that higher current rates on one side facilitate the charge phase, probably due to the lower size of the products, which means higher surface and in turn, in a solution-mediated process, it means that the reaction could happen more easily. On the other side, the high electrons mobility and in turn ions mobility required from high current tests complicates the formation and, more likely, the deposition of the products, leading to always lower discharge potential, till the short-circuit of the system.

Lower current rates instead seem to facilitate the deposition of the products, requiring a slow transfer of electron and thus increasing the time available for the products to recline on the porous cathode. However, the slowness of the discharge theoretically gives time to the products to form big cubic agglomerates which are then less likely to be dissolved when the charge phase happen. This result in a progressive accumulation of products on the cathode, which rapidly lead to an increase in the charge overpotential, pore clogging and finally to the cell failure.

Finally, since a reasonable operating time of a battery should be at least one hour (for real applications should be quite longer) we explored our best system with higher capacity. So we increased the time of charge and discharge to 1 hour, keeping the current rate to 0.2 mA, obtaining a capacity of 2000 mAh/g (see Figure 23).

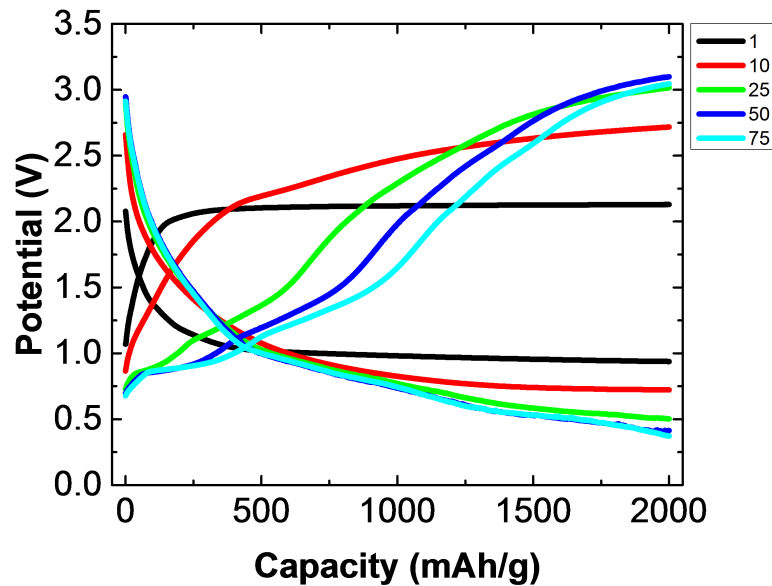
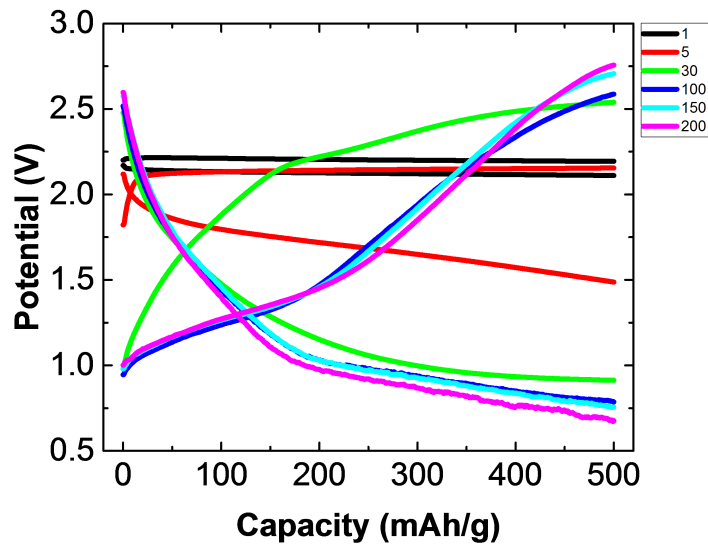


Figure 23: Shallow cycling of a Na – O<sub>2</sub> cell with 0.5 M of NaClO<sub>4</sub> dissolved in 90 % of TEGDME and 10 % of IL as electrolyte at 0.2 mA/cm<sup>2</sup>.

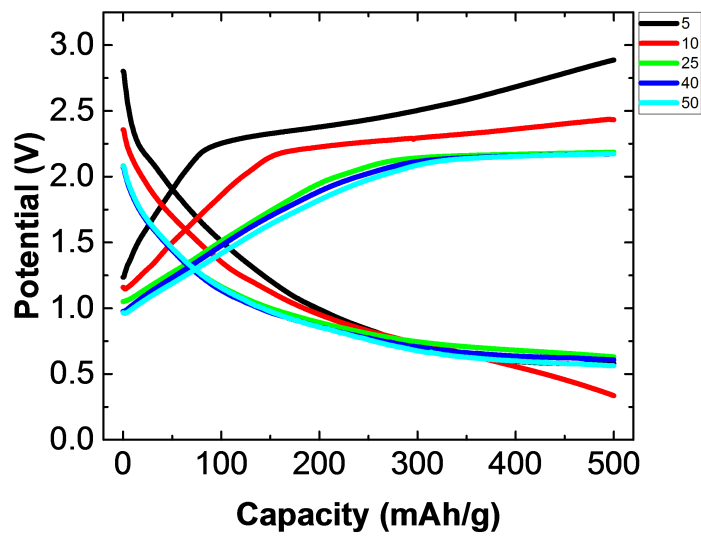
We obtained a system which ran for 75 cycles reaching a polarization gap of more or less 3.5 V. Thus the system could be explored also till high capacity, yet the performance need to be improved.

The second study we made was about salt concentration. Usually fairly low molarity of salts are dissolved in the electrolyte, i.e. from 0.1 to 0.5 M, however recently one group claimed the improved performance of the system at high salt concentrations up to 3 or 4 M. [33] Thus we decided to check which concentration of NaClO<sub>4</sub> at best enhance the performance of our battery. We performed all those experiments at a current rate of 0.1 mA. The first systems

tested were with high concentration: 1 M (Figure 24(a)), and 2 M (Figure 24(b)).



(a)



(b)

Figure 24: Shallow cycling of two Na – O<sub>2</sub> cells with EMIM – BF<sub>4</sub> and DMSO (in relation 1/9) as electrolyte at 0.1 mA/cm<sup>2</sup>, a) 1 M of NaClO<sub>4</sub>, b) 2 M of NaClO<sub>4</sub>.

We did not register any improvement, rather the cycles did not follow common behavior, which made us think that something wrong was happening, such as the reaction of the abundant salt instead of the pure sodium of the anode. Thus we abandon this road and we tested one cell with a lower concentration of  $\text{NaClO}_4$  than the normal one we used (0.5 M).

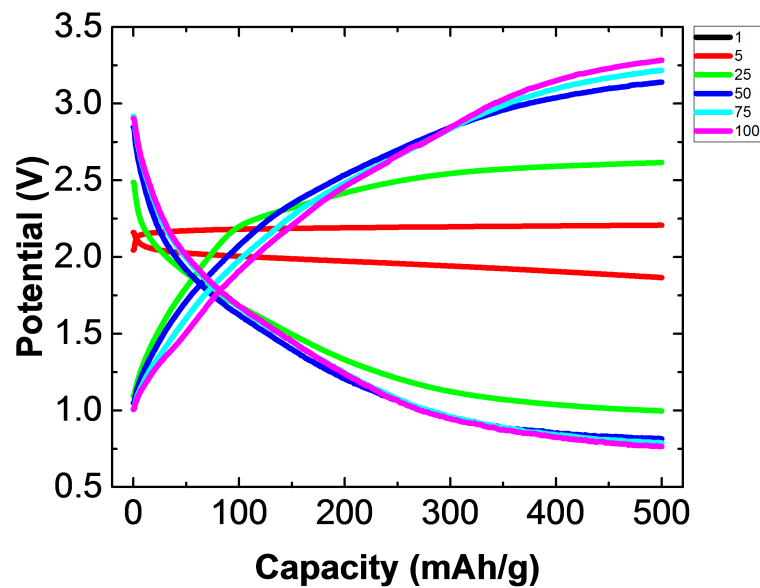


Figure 25: Shallow cycling of a  $\text{Na} - \text{O}_2$  cell with 0.1 M of  $\text{NaClO}_4$  dissolved in 90 % of TEGDME and 10 % of IL as electrolyte at  $0.1 \text{ mA/cm}^2$ .

From Figure 25 we see that the polarization gap grows fastly from 0.4 V after 5 cycles, to 2.5 V after 100 cycles, after that the cell failed. The performance are visibly worse than the one registered when the electrolyte with 0.5 M of salt was used. In fact in that case after 100 cycles the potential gap was about 2.0 V and the cell worked for other 100 cycles and it mantained this potential gap till and above the 150<sup>th</sup> cycle.

We concluded that the best concentration for our system must be around 0.5 M, yet deeper

studies need to be carried out to understand the precise molarity of salt and the exact role that it is playing, in order to avoid side-reactions or instabilities.

### 5.3 Anode Passivation

One of the main reasons which is believed to lead to the cell failure in Lithium–Oxygen is the dendrite growth on the anode, which culminates with the short-circuit of the battery. Many solutions could be experimented in order to block this growth and to avoid that lithium filaments to reach the cathode, yet the most promising alternative is the anodic protection through the formation of a passivated layer, i.e. a solid electrolyte interface (SEI).

It has been demonstrated that Li – O<sub>2</sub> cycle life could be enhanced by treating the anode with CO<sub>2</sub>. [34] The CO<sub>2</sub> reacts with Li to form Li<sub>2</sub>CO<sub>3</sub>, thus a layer of lithium carbonate mold on the anode, the so called SEI. This layer does not just avoid dendrite growth, but it also protects the anode from contamination and poisoning, which can occur when the metal comes in direct contact with the electrolyte or with oxygen ions (due to oxygen cross-over). These side-reactions are usually irreversible and lead to the formation of side-products which contaminate the system, increasing the resistances and ultimately leading to the cell failure. The amazing feature of this carbonate layer is the electrical and ionic conductivity, which let electrons and metal ions go through what acts like a wall for all the other species in the system. It is clear that this substrate increase the resistance of the system, and in turn the potential gap, but, on the other hand, it also incredibly enhance the stability of the cell. In fact in the long run a cell with a passivated anode overcomes the performance of a cell with a not-treated

anode also in efficiency.

In practice the anode passivation method consists in assembling one cell with  $\text{CO}_2$  instead of  $\text{O}_2$  for a few cycles. Then the battery is disassembled and, keeping the same anode, another cell is assembled with the normal system used, but with the passivated anode.

In particular, many studies has been carried out on this subject on  $\text{Li} - \text{O}_2$  and the most stable combination of electrolyte and salt for the passivation was revealed to be 0.5 M of Li-TFSI dissolved in 75 % of DMSO and 25 % of IL as electrolyte. Therefore we utilized the sodium counterpart of the salt, i.e. Na-TFSI, and the same combination of solvents for the cycles with the  $\text{CO}_2$ . On the other hand, when we reassembled the cell with the passivated anode, to make it works with oxygen, we came back to our best system, i.e. 0.5 M of  $\text{NaClO}_4$  dissolved in 90 % of TEGDME and 10 % of IL.

The important study which need to be performed is the optimization of the SEI thickness, which is strictly related to the number of cycles made with  $\text{CO}_2$ . Obviously, the more the anode is in the  $\text{CO}_2$  environment, the more it reacts, forming carbonate products, i.e.  $\text{Na}_2\text{CO}_3$ , and in turn, the more the passivated layer becomes thick. There is a optimum thickness which balance the protective function and the increase in resistance of the system. As far as concerns  $\text{Li} - \text{O}_2$  batteries, those number of cycles is claimed to be around 10; thus we started our study exactly imposing the cell to run for 10 cycles.

The shallow cycling of the system is reported in Figure 26.

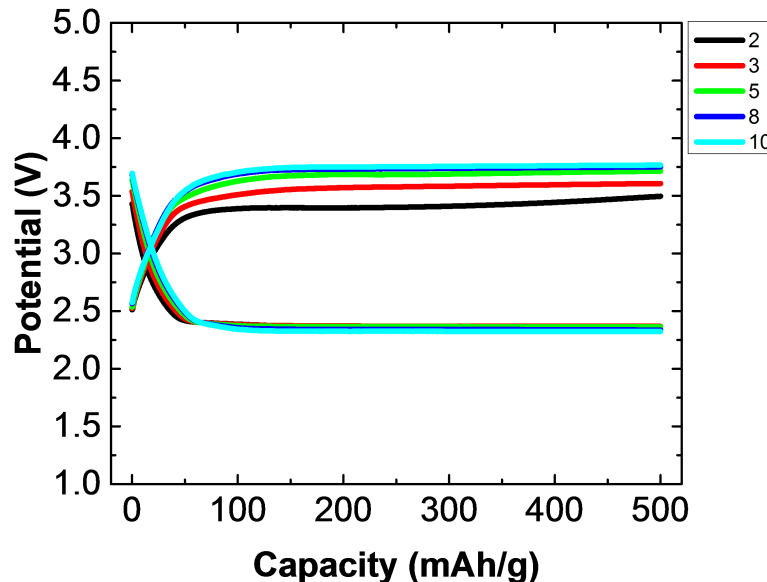


Figure 26: Shallow cycling of a Na – CO<sub>2</sub> cell with 0.5 M of Na-TFSI dissolved in 75 % of DMSO and 25 % of IL as electrolyte at 0.05 mA/cm<sup>2</sup>.

After that, we employed the treated anode to assemble a cell with our optimized combination of solvents and salt and we ran it at 500 mA/g. The characteristic curves of discharge and charge are reported in Figure 27.

As we see, the performance results markedly improved respect from the not-passivated counterpart, i.e. 15(b). In the first cycles the old result showed a lower polarization gap (up to  $\sim 0.5$  V in 10 cycles) than the new one (up to  $\sim 1$  V in 10 cycles), yet this is reasonable since the SEI layer, as already argued, increases the resistance of the system.

However, the situation is completely overturned from the 25<sup>th</sup> cycle on. The previous cell, i.e. not-passivated anode, had a potential gap of more than 2.0 V in the 25<sup>th</sup> cycle, and it increased quite sharply to more than 3.0 V in the 50<sup>th</sup> cycle and almost 4.0 V in the 100<sup>th</sup> and last cycle.

On the other hand, the new cell showed, as predicted, a more stable behavior. The 25<sup>th</sup> cycle is basically equal to the 10<sup>th</sup> one, i.e. a gap slightly higher than 1.0 V, and the more we cell ran, the more the detachment increased. In fact the 50<sup>th</sup> cycle had a potential gap which is half of the not-passivated cell, i.e.  $\sim 1.5$  V. Then the performance started to decrease more quickly, probably due to accumulation of side-products. After 100 cycles the gap increased to  $\sim 2.5$  V and during the 150<sup>th</sup> cycle it reached  $\sim 3.0$  V, just later the cell failed.

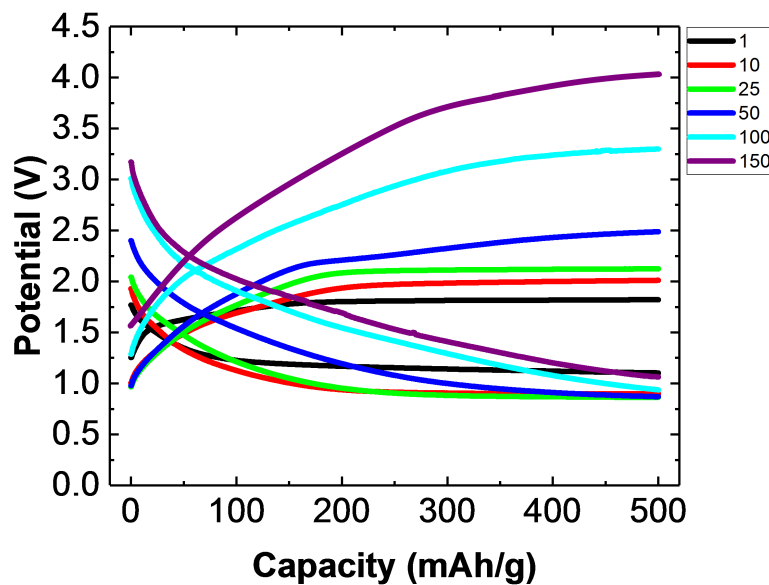


Figure 27: Shallow cycling of a Na – O<sub>2</sub> cell with 0.5 M of NaClO<sub>4</sub> dissolved in 90 % of TEGDME and 10 % of IL as electrolyte at 0.05 mA/cm<sup>2</sup>, after anode passivation.

In conclusion, as expected, the passivation of the anode increased the resistance for the first cycles, yet it also remarkably enhanced the stability of the system, resulting, in the long run, to increased performance. Thus, this method seems to be very promising to improve the

cycleability of the cell. However the thickness of the SEI layer still needs to be optimized and the stability of the species in the electrolyte remains a issue.

## CHAPTER 6

### CONCLUSION AND FUTURE WORK

We undertook a journey across the energy storage panorama, with a special focus on the future Me–air batteries and in particular Sodium–Oxygen system.

I outlined the properties which make Me–air the unborn successor of Li–ion and the main issues which are slowing down this transition. The best candidates and their principal features were explored, from Li – O<sub>2</sub> to Na – O<sub>2</sub> and K – O<sub>2</sub>, passing through Mg – O<sub>2</sub>, Al – O<sub>2</sub>, Fe – O<sub>2</sub>, and Zn – O<sub>2</sub>. Then we lingered on Na – O<sub>2</sub> batteries, pointing out the characteristics which make Sodium one of the best candidates for the practical development and consequent commercialization of a Metal–air battery, such as its low cost, its abundance on the Earth’s crust, and its high efficiency due to the one–electron transfer reactions. Afterwards we deepened the reported studies on products’ structure, conductivity, and stability of this system, as well as the proposed charge and discharge reactions path and the dependency on current rate of size, shape, and distribution of the products.

Finally we moved on the experimental work carried out, from the manufacturing of all the main components, i.e. anode, cathode, and electrolyte, to the actual assembly and testing of the cells. First we screened a wide range of combinations of electrolytes and salts, to find the one which works best in our system, that was 0.5 M of NaClO<sub>4</sub> dissolved in 90 % of TEGDME and 10 % of IL as electrolyte. We obtained a high efficiency in the first cycles (potential gap lower than

0.5 V) and a good cycleability (up to 100 cycles).

Second we performed a systematic study on how current rate influences the performance of our system. We showed how higher current rates facilitate the charge phase, but they complicate the formation and, more likely, the deposition of the products, leading to always lower discharge potential; while lower current rates seem to facilitate discharge, that results in the formation of bigger products and, in turn, higher energy required for the dissolution, i.e. for the charge phase.

Eventually we applied the anodic protection through CO<sub>2</sub> passivation, to enhance the stability of the cell and increase its cycle life, obtaining auspicious results.

It has been demonstrated that Sodium is one of the most promising applicant for the development of the battery of the future, however many issues still remains unsolved.

A deeper understanding of the reactions mechanisms is needed, as well as an enhancement of the stability of the electrolyte with anode and cathode. One road could be, for example, to continue the study on anodic passivation and to optimize it.

Moreover cathode should be designed accordingly to the requirements of the system, to improve the exploitation of the active sites and to favor deposition and dissolution of products. Ultimately other studies on current rate should be carried out, since it seems to greatly influence the operation of the system.

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## VITA

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EDUCATION	
	Master of Science in Mechanical Engineering, University of Illinois at Chicago, IL, USA, May 2017.
	Master of Science in Mechanical Engineering, Politecnico di Torino, Turin, Italy, July 2017.
	Bachelors degree in Mechanical Engineering, Politecnico di Torino, Turin, Italy, October 2015.
	Scientific High School Degree, Blaise Pascal, Giaveno, Turin, Italy, July 2012.
WORKING EXPERIENCES	
2011 - 2016	Tutor, Turin, Italy.
Oct 2015 – Jun 2016	Teaching Assistant, Politecnico di Torino, Turin, Italy.
Sep 2016 – May 2017	Research Assistant, University of Illinois at Chicago, Chicago, IL.
AWARDS AND CERTIFICATIONS	
2008	First place in the math contest "Giochi d'autunno", released by "Università Bocconi di Milano".
2010-2011	Partecipation at the math summer school, released by the Math Department of the University of Turin.
2011	ECDL (European Computer Driving License), released by "Associazione Italiana per l'Informatica e il Calcolo Automatico".
2015	SolidWorks Mechanical Design - Associate, released by "Dassault Systemes".
2015	SolidWorks Mechanical Design - Professional, released by "Dassault Systemes".
2016	Graduate fellowship, released by "Polythecnic of Turin" for the participation to the special program Top-UIC.

**VITA (continued)**

2017	Member of Honor Society of Phi Kappa Phi.
2017	Graduate scholarship, released by "Polythecnic of Turin" as a reward for the Master thesis work.

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**LANGUAGE SKILLS**

Italian	Native speaker
English	Professional working proficiency
French	Basic words and sentences only
Spanish	Basic words and sentences only

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**COMPUTER SKILLS**

Basic	Java, Adobe Illustrator, Photoshop, HTML.
Intermediate	Minitab, LATEX, Qform7, C++, Autodesk, AutoCAD, NX, MSC Adams, Origin.
Advanced	SolidWorks, Matlab, Microsoft Office.

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