

POLITECNICO DI TORINO Master's Degree in Nanotechnologies for ICTs

A.Y. 2022/2023

Master's Degree Thesis

$\mu {\rm SCs} \ {\rm for} \ {\rm Energy} \ {\rm Harvesting} \\ {\rm Fabrication} \ {\rm Processes} \ {\rm and} \ {\rm Perfromances} \\ {\rm Analysis} \ {\rm of} \ {\rm Metal} \ {\rm Oxides} \ {\rm Electroplating} \\ {\rm onto} \ {\rm LIG} \ {\rm Electrodes} \\ \end{array}$

Supervisor: Prof. Andrea Lamberti Co-Supervisor: Pietro Zaccagnini

Student: Sperti Marco

A Paola,

che semplicemente mia sorella.

la mia armatura contro le difficoltá di questo percorso, per avermi insegnato la passione e la determinazione, per aver mantenuto la promessa di non fare stupidaggini fino al mio ritorno ogni volta che andavo via, per essere stata sempre molto piú

Abstract

Due to their high power density, rapid charge and discharge capabilities, and long lifetime, Micro-Supercapacitors (μ SC) have garnered significant interest for their possible utilization for energy harvesting in micro and integrated electronics. The effort in this work lies in the optimization of materials and in manufacturing processes of their electrodes rather than in their integration methods with other micro devices to obtain more smart and complex systems.

The interfacial properties of thin film Transition Metal Oxides (TMOs) will be studied for this aim. Their high surface area and easy deposition technique (electroplating) make them an excellent candidate as a cathode and anode for μ SC. Laser Induced Graphene (LIG) will be used as substrate, and so, its great electronic properties and cheap, fast and green fabrication methods.

The final aim of this research work is to realize an asymmetric device in order to exploit the properties of two different TMOs for the two electrodes of the SC and extend its operating voltage window in aqueous electrolyte, aqueous electrolyte.

Keywords: Microsupercapacitors, Tranistion Metal Oxides, Laser Induced Graphene, Asymmetric Device, Electroplating, Aqueous Electrolyte

List of Figures

1.1	Supercapacitors as Energy Storage Devices	2
1.2	Physical phenomena behind SCs and relative used materials	3
1.3	Electric Double-Layer (EDL)	4
1.4	deflection angle α_B of the flexible μ SC	7
1.5	Allotropes of Carbon	8
1.6	Graphene: spatial and reciprocal lattice	9
1.7	Graphene Energy Spectrum $E = E(k) \dots \dots \dots \dots \dots \dots$	10
2.1	DLW System	20
2.2	Cross Section of the steps of the Electroplating Process	23
2.3	Electroplating experimental setup	24
2.4	Reference Electrode	25
2.5	Platinum Counter Electrode	26
2.6	Electroplating Cell	27
2.7	Electroplating Experimental Setup	27
2.8	Balance used for the mass evaluation	29
2.9	Working principle of Scanning Electron Microscopy	31
2.10	FESEM equipment	32
2.11	Schematic of a XPS equipment	34
2.12	EC Characterization: experimental setup	36
2.13	Electrochemical Cell	36
2.14	Equivalent Circuit of the electrochemical cell in full cell configuration	37
2.15	Active Carbon CE fabrication steps	38
2.16	Equivalent circuit describing the physical phenomenon	41
2.17	Simplest Circuit Model for a SC	41
2.18	Nyquist Plot for a Supercapacitor's electrode	42
2.19	CV signals and results	43
2.20	Charge/Discharge	43
2.21	Pouch Cell	46
2.22	Cross Section of the Experimental Setup for Device Characterization	47
2.23	Schematic of the Pouch Cell (Cross Section)	47
2.24	Schematic of the Pouch Cell (Top View)	48
2.25	GCD - Control Signal	49
3.1	LIG electrodes	51



3.2	Sulfates X_2SO_4 used as Support Salts	52
3.3	Electroplating Solution	53
3.4	Samples before the plating process (Active Area: LIG only)	54
3.5	Electroplating - Plots of the main quantities	54
3.6	CV comparison between LIG blank and LIG after the electroplating .	56
3.7	EC characterizations for electrodes with LIG only and MnO_2	
	electrodeposited at different deposition time. [18]	57
3.8	Potential vs time for the calibration plot for the MnO deposition	58
3.9	Calibration plot for the MnO deposition	59
3.10	FESEM. Na-MnO	60
3.11	FESEM. Li-MnO	61
3.12	Electrodes immediately afterwards the EC characterization in	
	Na_2SO_4 1 M electrolyte	62
3.13	FESEM. K-MnO	62
3.14	XPS. Survey spectrum	63
3.15	XPS. HR spectrum for Manganese	64
3.16	XPS. HR spectrum and deconvolution for Manganese	65
3.17	OCV plots - Manganese Oxide electrode	66
3.18	CV plots - Manganese Oxide electrode	67
3.19	CV Parameters as a function of cycle number - NaMnO electrode	68
3.20	Nyquist plots from EIS - NaMnO electrode	68
3.21	CV plot for each support salt (last cycle)	70
3.22	EIS plot for each support salt (after CV)	70
3.23	Specific Capacitance vs. Ionic Radius	71
3.24	$Na_{0.55}Mn_2O_4 \cdot 1.5H_2O$ schematic illustration and structural analysis	
	of the nanosheet and its counterpart [43]	72
3.25	LIG rectangular features. Active Area = $0.25 \text{ cm}^2 \dots \dots \dots \dots$	73
3.26	Thermal Process during time	73
3.27	Electrodes synthesized with: Electroplating at 1 mA $\rm cm^{-2}$ and	
	Calcination at several t_{calc}	74
3.28	Self discharge profiles of Positive (Solid Lines) and Negative (Dashed	
	Lines) charged electrodes of (a) Carbon in 1 M aq. H_2SO_4 , (b) RuO_2	
	in 0.5 M aq. H_2SO_4 and (c) MnO in 0.5 M aq. Na_2SO_4	77
3.29	Temporal evolution of the self discharge measurement method by	
	varying t_f	80
3.30	Self discharge - Potential vs time, measured for blank electrode in	
	different atmospheres	81
3.31	Self discharge: Potential Energy Loss during the SD time vs t_f for	
	blank electrode	81
3.32	Measurement cell with N_2 flux	82
3.33	Self discharge - Potential vs time, measured for blank electrode in	
	different atmospheres	82
3.34	Self discharge: Potential Energy Loss during the SD time vs t_f for	
	blank electrode in different atmospheres	83



3.35	Self discharge - Potential vs time, measured for MnO electrodes.
	Electroplating: positive current, calcination: 2h, 300°C
3.36	Self discharge: Potential Energy Loss during the SD time vs t_f for
	blank and MnO electrodes in air
3.37	CV measurement for different atmospheric condition
3.38	Self discharge measurements
3.39	Cross Section of the Electrode after the FeO Deposition
3.40	Iron Oxide electroplating solution
3.41	Iron Oxide Electroplating. TEST 1
3.42	Iron Oxide Electroplating. TEST 2
3.43	Potential vs time for the calibration plot for the FeO deposition 90
3.44	Calibration plot for the FeO deposition
3.45	FESEM - FeO
3.46	CV Characterization - FeO (TEST 1)
3.47	EIS Characterization - FeO (TEST 1)
3.48	EC Characterizations - FeO (TEST 1 & 2)
3.49	EC Characterizations - FeO (TEST 3)
3.50	Rectangular geometry - CAD design with Rhinoceros
3.51	LIG - Planar device geometry
3.52	Preparation of the device for the electroplating process
3.53	CV plots - MnO FeO electrodes in Li_2SO_4 , 0.5 M $\ldots \ldots 99$
3.54	Cross Section of the device during the FeO and MnO deposition 100
4.1	OCV Characterization - Sandwich Device: (+) LIG MnO 0.5 M
	$Li_2SO_4 FeO LIG(-)$
4.2	GCD Characterization - Sandwich Device: (+) LIG MnO 0.5 M
	$Li_2SO_4 FeO LIG(-) \dots \dots$
4.3	GCD Characterization: Capacitance retention and Efficiencies -
	Sandwich Device: $(+)$ LIG MnO 0.5 M Li ₂ SO ₄ FeO LIG(-) 103
4.4	CV plots - Devices in Pouch Cell Configuration
4.5	CV Characterization: Capacitance retention and efficiencies - Device
	$D_{1,500\mu m}$: (+) LIG MnO 0.5 M Li ₂ SO ₄ FeO LIG(-) 104
4.6	Nyquist plots - Device in Pouch Cell Configuration
4.7	GCD Characterization - Pouch Cell Device: (+) LIG MnO 0.5 M
	$Li_2SO_4 FeO LIG(-)$. Capacitance Retention
4.8	GCD Characterization - Pouch Cell Device: $(+)$ LIG MnO 0.5 M
	$Li_2SO_4 FeO LIG(-)$. Coulombic and Energy Efficiency 106
4.9	Areal Ragone plot for graphene's electrodes used in μ SCs by using
	Laser and Non-Laser technologies



4.10	Areal Ragone plot for a cellular graphene based μ SC and a quasi-
	solid-state μ SC in comparison with μ SCs based on different types
	of active materials, including laser reduced graphene, graphene
	quantum dots, reduced GO/CNT, thermally reduced graphene,
	vertically aligned graphene, graphene/phosphorene hybrid films,
	photochemically reduced graphene, S-doped graphene film, laser-
	processed graphene and CVD graphene/CNT carpets hybrid materials 108
4.11	Areal Ragone plot for $LIG FeOOH//LIG MnO_2$, $LIG MnO_2$ -2.5h and

LIG PANI-15														•								•										109)	
-------------	--	--	--	--	--	--	--	--	--	--	--	--	--	---	--	--	--	--	--	--	--	---	--	--	--	--	--	--	--	--	--	-----	---	--

List of Tables

2.1	Electroplating - Parameter	28
2.2	OCV - Parameter	39
2.3	EIS - Parameter	40
2.4	CV - Parameter	42
2.5	GCD - Parameter	49
3.1	Support Salt parameters	53
3.2	Manganese Oxide (support salt variation) - Amount of deposited	
	material	55
3.3	Manganese Oxide, support salt variation - Mean value of the amount	
	of deposited material and electroplating efficiency	55
3.4	MnO calibration plot measurements	58
3.5	XPS. Manganese Peaks	64
3.6	XPS. Manganese Peaks for $Mn(III)$ and $Mn(IV)$ contributions \ldots	65
3.7	Electrode Parameters - X-MnO	69
3.8	Electrode Parameters - support salt comparison	69
3.9	ZIB cathode - Capacity. [43]	72
3.10	Iron Oxide - TEST 1. Amount of deposited material	88
3.11	Iron Oxide - TEST 2. Amount of deposited material	89
3.12	FeO Calibration Plot measurements	91
3.13	Electrode Parameters - FeO (TEST 1)	94
3.14	Electrode Parameters - FeO (TEST 2)	95
3.15	Electrode Parameters - FeO (TEST 3)	96
3.16	Device - Amount of deposited mass	101
4.1	Device Parameters	105

Contents

1	Intr	roduction 1
	1.1	Supercapacitors & Energy Storage Device 1
	1.2	μ SC - Micro Supercapacitors
	1.3	Materials
		1.3.1 LIG - Laser Induced Graphene
		1.3.2 TMOs - Transition Metal Oxides
2	Met	chods 20
	2.1	Direct Laser Writing Procedure
	2.2	Electroplating
	2.3	Material Characterization
		2.3.1 FESEM
		2.3.2 XPS
	2.4	Single Electrode - Electrochemical Characterization
		2.4.1 Experimental Setup
		2.4.2 Techniques
	2.5	Device - Electrochemical Charcterizations
		2.5.1 Pouch Cell
		2.5.2 Electrochemical Characterization Techniques
3	Res	ults 51
-	3.1	Single Electrode Fabrication & Characterization
		3.1.1 MnO Electrode - Anode
		3.1.2 FeO Electrode - Cathode
	3.2	Device Fabrication
	-	3.2.1 CAD Design and LIG process
		3.2.2 Charge Balancing
		3.2.3 Electroplating
4	Dise	cussion 102
-	4.1	Device Characterization
	4.2	Comparison with Literature
	4.3	Conclusions
•		1
A	ppen	uix 112

Chapter 1

Introduction

1.1 Supercapacitors & Energy Storage Device

The urgent need to explore renewable energy sources and related technologies for energy generation, storage, and conservation is driven by the negative, long-term consequences of greenhouse gas emissions and the finite supply of fossil fuels. One significant challenge is the dependence on power lines for electricity distribution. While wireless power supply concepts have been investigated, they are mainly experimental and unlikely to have a major impact soon. Another hurdle is ensuring the stability and reliability of electricity generated from wind and solar energy sources.

The demand for power storage, conversion, transportation, and supply across different scales has led to substantial research and exploration. As a result, various *Electrical Energy Storage (EES)* technologies have been developed to address these needs. [46] Some of these technologies, such as batteries and fuel cells, are commonly used in our everyday lives. Others, such as pumped hydro, flywheel, compressed air, superconducting magnetic, and *Supercapacitors*, are primarily employed in industrial applications.

Batteries, both rechargeable and non-rechargeable, are crucial energy storage technologies that operate through redox reactions. They have gained widespread usage and continuous research focus since the 20th century, becoming an integral part of our daily lives. However, there are certain areas where batteries have shown limitations or failed to meet certain requirements, including: [46]

- Low Power Density: this drawback significantly hampers applications that demand high power discharge or recharge rates.
- Heat Generation: redox reactions within batteries can result in Joule heating and thermochemical heating during their operation. If not effectively dissipated, this heat can lead to overheating, thermal runaway, and even fire.
- Limited Cycle Life: batteries typically have a limited number of discharge and recharge cycles due to the lack of fully reversible redox reactions throughout the process.



Figure 1.1: Supercapacitors as Energy Storage Devices. In (a) Ragone Plot of Supercapacitors and other EES technologies. In (b) Simple Supercapacitor structure schematic

Batteries alone are not enough for addressing energy storage challenges. There's a need for advanced, high-performance energy storage devices to revolutionize power systems in various sectors. Substantial efforts are directed towards their development.

Supercapacitors (SCs), also known as ultracapacitors or electrochemical capacitors, exhibit remarkable power performance, exceptional reversibility, and an exceptionally long cycle life surpassing one million cycles. They operate through a straightforward mode and can be seamlessly integrated into electronic systems, showcasing their ease of use and integration. Moreover, SCs generate minimal thermochemical heat due to their simplified charge storage mechanisms. They also have low internal resistance, wide operating temperature window. and high efficiency. [46]

As a result of these advantages, SCs have found wide applications in consumer electronics, memory backup systems, and industrial power and energy management. Additionally, supercapacitors (SCs) are expected to enter even more specialized markets in the near future, broadening their applications and influence. Fig.1.1(a) illustrates a comparison between SCs and batteries, highlighting SCs' ability to deliver significantly higher power density, enabling faster energy release, and their superior energy storage capacity compared to traditional capacitors.

Structurally, as can be seen from Fig.1.1(b), the SC consists of two electrodes, an electrolyte as dielectric material and membrane separator. Current collectors are used to withdraw the current from the electrodes and to study it. The physical behaviour behind such devices stores charge can be summarized in two main phenomena: [46]

- Electrostatic storage: Electric Double-Layer (EDL)
- Electrochemical storage: Pseudocapacitive effect



Figure 1.2: Physical phenomena behind SCs and relative used materials

Depending on the material and on the design of the electrodes of the Supercapacitor, it can work through one of them or through a mix of these two effects: *hybrid* SC. The difference stands in the charge storage mechanisms, as shown in the diagram of Fig.1.2.

Regarding the design, the current collectors must be high conducting materials, the electrolyte must not degrade in the potential window used for the device and must be chosen accordingly, the membrane separator must avoid short circuit and allow the ion mobility and the electrodes have to store charge by exploiting these effects. The SCs research pushes a lot on the exploration of different materials to investigate all the possible advantages and disadvantages.

EDL. A EDL manifests when an object, for example a solid particle or a body with a porous surface, comes in contact with a fluid. It refers to the existence of two parallel layers of charge that surround the object. It represents an electrostatic equilibrium between charges in the solid and charges in the liquid. Within the liquid, there are two main components of the electric double layer (EDL): the *Outer Helmholtz Plane, OHP* that is the first layer of ions closest to the solid interface and the *Diffuse Layer* that is to say the second layer that extends into the liquid environment like a "tail." In addition to these, there's the *Inner Helmholtz Plane (IHP)*, consisting of charges and solvent molecules even closer to the solid interface, often without selective adsorption. The IHP forms a narrower layer of molecules and charges near the solid-liquid interface, playing a crucial role in electrochemical dynamics and interactions between the solid and liquid.

The most important result of this effect is the formation of two layers with opposite polarity, and so, a capacitance at the interface between the solid phase (the electrode, in our case) and the liquid phase (the electrolyte). A simple schematic of the EDL effect is shown in Fig.1.3, where also the potential distribution is reported



as a function of the distance in the liquid, starting from the electrode. It can be demonstrated that this potential will decay exponentially with the law:

$$\phi(z) = \zeta e^{-\frac{z}{\lambda_D}} \tag{1.1}$$

where ζ is the value of the potential at z = 0 and depends on the solid-liquid interface, while λ_D is a characteristic length called Debye Length that depends on some parameters as the diffusivity D, the conductivity σ and the dielectric constant ϵ of the liquid.



Figure 1.3: Electric Double-Layer (EDL)

The concept of the *Electric Double-Layer (EDL)* phenomenon was initially introduced by Helmholtz in 1853 and it was later patented by Becker of General Electric Company in 1957. Becker utilized porous carbon material with a high specific area to create electrodes that facilitated the formation of a double-layer structure. The capacitive performance of the electrode in Electric Double Layer Capacitors (EDLCs) depends on the properties of the electrolyte, which must be tailored for optimal performance. EDLCs use high-surface-area activated carbon (AC) to store a large amount of charge, measured in Farads (F), unlike traditional capacitors measured in picofarads (pF) or microfarads (μ F).

Pseudocapacitance. It emerges at the surfaces of electrodes where charges are stored through faradaic processes. This charge storage mechanism, which is based on a redox process, can make the electrode material behave somewhat like a battery in terms of its reaction behavior. [12] However, the electrochemical characteristics are distinct: in these supercapacitors, you typically observe psuedo-rectangular cyclic voltammograms (CVs) and nearly linear galvanostatic charge-discharge (GCD) curves, resembling those of electric double layer capacitors (EDLCs). These signatures indicate rapid faradaic reactions that are not constrained by solid-state diffusion, setting supercapacitors apart from batteries. [46, 44]

This phenomenon arises due to thermodynamic factors, as the faradaic charge transfer occurring across the electric double layer results in a potential-dependent accumulation or release of charge. These devices are referred to PCs. During the charging process, the surface region of redox-active electrode materials, undergoes reduction, resulting in a decrease in their oxidation states. At the same time, cations from the electrolyte are adsorbed or inserted near the electrode surfaces. Upon discharge, this process can be nearly fully reversed.

- Transition metal oxides (*TMOs*), such as RuO₂, MnO₂, and FeO₂, exhibit rapid and reversible redox reactions on their surfaces, displaying strong pseudocapacitive behavior. [44] This reversibility is evident in cyclic voltammetry (CV) curves, which showcase symmetric redox peaks, in contrast to the rectangular CV curves seen in electric double layer capacitors (EDLCs). These transition metal oxides have been extensively studied due to their high capacitance, which often significantly surpasses the double-layer capacitance achievable with carbon materials.
- Transition Metal Nitrides (TMNs) like TiN, Mo₂N, NbN, and VN are promising pseudocapacitive materials due to their large specific capacitances and high electronic conductivities. [10, 44] VN's high density also provides a large volumetric capacity for energy storage, which is beneficial for micro supercapacitors. The pseudocapacitance mechanism of transition metal nitrides (TMNs), such as VN, is still unclear and subject to debate. Some suggest it involves surface Faradaic reactions involving oxynitride (VN_xOy) or nitride species, while others propose a different mechanism involving charge conversion of V³⁺ to V²⁺.
- Layer-structured Metal Dichalcogenides like SnS and MoS₂ have shown impressive rate performance in sodium-ion batteries because of their pseudocapacitive sodium storage mechanisms. [7] The exact reasons for pseudocapacitance in materials like SnS₂ are not fully known. It's hypothesized that SnS₂, with its unique structure, could offer high pseudocapacitance for use in sodium hybrid capacitors (SHCs) to achieve high energy density. To make the most of SnS₂'s pseudocapacitance, two things are crucial: a highly conductive carbon support for efficient electron transport and a large surface area on SnS₂ to store sodium ions effectively and maximize energy storage capacity.
- High conductivity is crucial for pseudocapacitive materials. *Conducting Polymers* achieve this by having charge carriers, charge mobility, facile kinetics, and available solvated counterions. [6] Conducting polymers form charge "islands" when ionized, with shifts in energy levels and new energy bands in the material's band gap. However, their one-dimensional nature leads to a Peierls distortion, known as a Jahn Teller like relaxation, causing a segregation between filled and unfilled portions of the sp² band, which influences their conductivity.

These mechanisms coexist within SCs and make varying contributions to the overall charge storage capacity. The relative proportions of these mechanisms can differ depending on the specific design and materials used in the SC.

Finally, *Hybrid Capacitors (HCs)* have been developed by combining capacitive electrodes from EDLCs and/or PCs with battery electrodes. This combination aims to enhance the energy storage capacity by maintaining high power performance. For example, [7] aqueous supercapacitors excel in delivering high power densities but fall short when it comes to achieving high energy densities. The hybrid approach aims to leverage the strengths of both mechanisms to achieve a balance between high power and high energy density in supercapacitor technology.

In line with numerous other areas of research, graphene and graphene-like materials have garnered considerable interest in the field of SCs. This is primarily due to their exceptional electron transport properties and remarkable surface area. Additionally, these materials offer the advantage of easy preparation of various nanoscale morphologies. Moreover, the fabrication processes for graphene-based supercapacitors are cost-effective and environmentally friendly. The unique combination of these attributes has propelled graphene and graphene-like materials to the forefront of supercapacitor research.

1.2 μ SC - Micro Supercapacitors

The development and miniaturization of energy storage devices are driving progress in modern microelectronics. Currently, microbatteries are the primary power source for micro electronic devices, despite their limitations such as slow charge/discharge rates and a limited cycle life. In contrast, microsupercapacitors (μ SCs) offer advantages like high power density, fast charge/discharge rates, and long service life. Their in-plane interdigitated electrodes suggest they could replace microbatteries.

However, creating easily manufacturable μ SCs with high energy densities, comparable to or surpassing microbatteries, without compromising other electrochemical properties is a significant challenge. A common approach, following the scheme of Fig.1.2, is to use photolithography to create interdigitated patterns of highly conductive carbon materials, enhancing electrochemical double layer capacitance (EDLC). Laser writing technology has also been employed to pattern and reduce graphene oxide (GO) as interdigitated electrodes in μ SCs. However, challenges in GO synthesis, post-reaction treatment, and GO stability in these devices pose commercialization hurdles. The energy density of the device is $E = \frac{1}{2}CV^{2}$. It depends on capacitance and working voltage. Enhancements in capacitance involve, from Fig.1.2, the use of pseudocapacitive materials like Transition Metal Oxides (TMOs) and Conductive Polymers, but they often entail costly or harsh processes. Another approach is using organic electrolytes to increase the operating voltage window, but this has safety and fabrication challenges. [18]

The possible solution that will be studied during this work is to create **asymmetric** μ **SCs** without organic electrolytes. Porous and multilayered graphene will be patterned onto a polymide substrate by exploiting Laser Writing to obtain

 μSCs

Politecnico di Torino

Laser Induced Graphene (LIG), and it will be used as substrate for the TMOs deposition, or eventually conductive polymers (but they will not be used for this work), different for anode and cathode, to obtain the asymmetry of the device.

Another important advantage that can be had in manufacturing μ SCs using Laser Writing is the possibility to obtain very precise patterns and avoiding short circuits already during the fabrication phase and not by using a membrane as separator. Furthermore, the dimensions and geometries of the electrodes can be designed using CAD computer software.

Several material characterization as SEM, XRD, XPS, Raman must be done on the resulting LIG-TMOs electrodes to observe the very important interfacial properties and morphology to enhance their capacitive performances.

The polymide substrate for LIG formation and the choice of the deposited metal oxides will also offer high flexibility. The image of Fig.1.4 shows the device bent by hand at a certain angle α_B and it has been demonstrated [18] that, for LIG-MnO₂ electrodes, the differences in the capacitive performances of the device by modifying this parameter are negligible. The good mechanical flexibility has been further demonstrated by the well maintained morphology of LIG-MnO₂ after bending tests compared to the original one.



Figure 1.4: deflection angle α_B of the flexible μ SC [18]

Finally, the last crucial information about the design and fabrication of the desired device is the electrolyte's selection. Aqueous electrolytes will be used for this work, and this choice will have consequences on the applied voltage window.

For what concern the performances evaluation, in contrast to traditional supercapacitors for which the performances are typically evaluated based on the weight of the active material, the primary consideration for μ SCs is their footprint area. This shift in focus makes spatial energy and power density the most crucial performance metrics for μ SCs. Essentially, it's about optimizing the energy and power storage capacity within a confined physical space, which is critical for their integration into miniaturized electronic devices.



1.3 Materials

A brief description of the materials used during this work will be done in this section, by discussing physical and chemical properties, their technological fabrication methods and their main applications.

1.3.1 LIG - Laser Induced Graphene

Graphene



Figure 1.5: Allotropes of Carbon

Graphene is one of the carbon allotropes, an extremely thin material, theoretically one layer, consisting of carbon atoms arranged in a two-dimensional hexagonal pattern, that is the result of the bonds between the C atoms.

Chemical Bonds Carbon *C* has six electrons, with four being valence electrons. Initially, two occupy 2s-orbitals, and two occupy 2p-orbitals. When one 2s-electron moves to 2p, they combine, forming sp^2 hybrid orbitals, leading to three such orbitals. These sp2-hybridized electrons create σ -bonds when they connect between carbon atoms in graphene, forming a robust hexagonal lattice. The angle between these bonds is about 120, and their distance is 1.42 Å. Additionally, unhybridized p-orbitals overlap to create π -orbitals, allowing electrons to move freely, giving graphene its exceptional conductivity. [4, 25]

Crystal Structure The graphene direct lattice is shown in Fig.1.6 (left). It consists of two interpenetrating sublattices (black and blank points), each of them forming a triangular Bravais lattice. It can be genrated by a linear combination of two primitive vectors $\vec{a_1}$ and $\vec{a_2}$ defined as:

$$\begin{cases} \vec{a_1} = \begin{pmatrix} 1\\ 0 \end{pmatrix} a \\ \vec{a_2} = \begin{pmatrix} \frac{1}{2} \\ \frac{\sqrt{3}}{2} \end{pmatrix} a \end{cases}$$

where a is the distance between two neighbouring points of the same sublattice, and is related to the distance d of two carbon atoms by $a = \sqrt{3}d = 2.46$ Å. [4, 25]



Figure 1.6: Graphene exagonal (or honeycomb) spatial lattice (left) and reciprocal lattice (right)

By putting the origin at the center of an hexagon, the position of the blank and black points can be written by exploiting the two translation vectors:

$$\vec{v_1} = \begin{pmatrix} 0\\1 \end{pmatrix} \frac{a}{\sqrt{3}} = -\frac{1}{3}\vec{a_1} + \frac{2}{3}\vec{a_2}$$

$$\vec{v_2} = \begin{pmatrix} 0\\-1 \end{pmatrix} \frac{a}{\sqrt{3}} = \frac{1}{3}\vec{a_1} - \frac{2}{3}\vec{a_2}$$
 (1.2)

So, the coordinate \vec{x} for a black or a blank point can be written as:

$$\vec{x_{\bullet}} = n_1 \vec{a_1} + n_2 \vec{a_1} + \vec{v_1} \qquad n_1, n_2 \in \mathbb{Z} \vec{x_{\circ}} = n_1 \vec{a_1} + n_2 \vec{a_1} + \vec{v_2} \qquad n_1, n_2 \in \mathbb{Z}$$
(1.3)

The reciprocal lattice (Fig.1.6, right picture) can be obtained from the Direct one by using the Laue Condition:

$$exp(i\vec{k}\cdot\vec{x}) = 1 \tag{1.4}$$

where \vec{k} is a vector in the reciprocal lattice that can be expressed, as usual, as a linear combination of two primitive vectors $\vec{b_1}$ and $\vec{b_2}$. By using Eq.1.4, they can be written as a function of the *a* parameter:

$$\begin{cases} \vec{b_1} = \binom{\sqrt{3}}{2} \frac{4\pi}{\sqrt{3}a} \\ \vec{b_2} = \binom{0}{1} \frac{4\pi}{\sqrt{3}a} \\ \vec{k} = m_1 \vec{b_1} + m_2 \vec{b_1} \qquad m_1, m_2 \in \mathbb{Z} \end{cases}$$
(1.5)

9

Politecnico di Torino

Physical Properties It has attracted significant attention across various research fields due to its exceptional properties: [29, 48, 17, 30]

- Exceptional Properties. It has garnered significant attention due to its outstanding characteristics, including high thermal conductivity (4840 5300 W m⁻¹ K⁻¹), excellent light transparency (97.4%), remarkable mechanical strength (1 TPa), and a large surface area (2630 m² g⁻¹).
- Unique Transport Properties. Graphene's electronic energy spectrum is distinctive (Fig.1.7). Because of its honeycomb lattice structure, electrons in graphene behave as massless quasi-particles, following the Dirac equation instead of the Schrödinger equation. Mathematical methods like Hamiltonian diagonalization through the Hubbard Model or Effective Low-Energy Field Theory [4, 25] help to describe this spectrum.



Figure 1.7: Graphene Energy Spectrum $E = E(\mathbf{k})$

- Ultra-Thin Layer. Graphene consists of a single atom-thick layer, making it accessible and adaptable to various scanning probes. It is highly sensitive to adjacent materials, including dielectrics, superconductors, and ferromagnetics, offering versatile possibilities compared to conventional two-dimensional electronic systems.
- *Resilience to Scattering.* Graphene's electrons can traverse submicrometer distances without experiencing scattering, even when placed on rough substrates and covered with adsorbates at room temperature. This exceptional behavior underscores graphene's high electron mobility and suitability for electronic applications.
- Quantum Effects. Graphene's massless electrons exhibit robust quantum effects that can persist at room temperature, with electron mobility reaching very high values ($\mu_e \sim 2 \cdot 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).

All these unique qualities, which distinguish graphene from its bulk structure, graphite, open up exciting new possibilities for several applications.

Graphene - Fabrication Techniques

Conventional Techniques and their drawbacks. Numerous methods [16] have been developed for the production of graphene, including mechanical exfoliation of graphite, chemical vapor deposition (CVD) using gaseous hydrocarbons on solid substrates, epitaxial growth on silicon carbide crystals, and reduction of graphene oxide (GO). However, these conventional approaches often come with drawbacks such as low productivity, demanding preparation conditions, high energy consumption, and the generation of substantial chemical waste. Moreover, the need for cost-effective and scalable graphene production presents challenges in the pursuit of alternative technologies.

Direct Laser Writing (DLW). Direct Laser Writing (DLW) offers a fascinating approach to induce graphenization in specific polymers by harnessing their remarkable ability to absorb long wavelength radiation, resulting in photo-thermal and photo-chemical effects. [14] It offers several advantages: unlike traditional methods, DLW eliminates the need for masks, lithography, and the use of toxic etching chemicals. [14, 16] DLW offers design flexibility, productivity, and eco-friendliness in manufacturing processes. It allows for precise and rapid fabrication, is suitable for micro and nanofabrication, and is environmentally friendly due to non-contact processing and low energy consumption. Additionally, DLW is cost-effective, scalable, and compatible with 3D structures.

The exploration of laser ablation of polymers began in the early 1980s. This technique, particularly effective on polyimide surfaces, gives rise to the formation of Laser Induced Graphene (LIG), a distinctive nanostructured and porous carbon network. In the LIG formation process, laser energy raises localized temperatures, causing lattice vibrations and breaking atomic bonds in the polymer chains. These freed atoms can recombine or turn into gases, creating high pressure and contributing to LIG's porous structure. [16] The emergence of LIG opens up exciting possibilities for a wide range of applications, thanks to its exceptional properties and versatility. The morphology and the physical properties of the resulting material will be different depending on the process parameters of the Laser: power, scan speed, frequency of the incident radiation, etc...

Laser technologies. LIG fabrication can be achieved using various types of lasers. [16]

- CO_2 Lasers. They have been developed in the early 1960s and have been widely applied in laser machining. They have found extensive use in the fabrication of LIG. The advantages of this kind of laser are the high output power and the low cost per watt. Their beams are characterized by a wavelength ranging from 9 to 11 μ m, absorbed by the C-C bonds in carbon precursors.
- Nd: YAG Lasers. Neodymium-doped Yttrium Aluminum Garnet solid-state lasers, emitting at 1064 nm wavelength are used in metal manufacturing. Both



continuous-wave and pulsed Nd:YAG lasers are used to make laser-induced graphene (LIG) from polyimide. Continuous-wave lasers yield around 40 Ω sq⁻¹ Sheet Resistance, but it's not as good as the 15 Ω sq⁻¹ achieved with CO₂ lasers. Neodymium-doped yttrium aluminum garnet (Nd:YAG) solid-state lasers, emitting at a wavelength of 1064 nm, have been developed alongside CO₂ lasers for the metal manufacturing industry.

• Semiconductor Diode Lasers. Semiconductor diode lasers were invented in the early 1960s and gained attention in the 1990s as possible replacements for CO₂ and Nd:YAG lasers in material processing. They offer several advantages, including a wide range of available wavelengths, from 405 nm for InGaN blue violet laser to 3330 nm for GaInAsSb laser, and high electrical to optical conversion efficiency up to 50% compared to Nd:YAG.

Visible diode lasers are cost-effective, offer high spatial resolutions, typically 6 to 12 μ m, and have good absorption properties for carbon precursors. These advantages suggest an increasing use of diode lasers in fields where laser-induced graphene (LIG) is applied in the future.

• *Fiber Lasers.* Fiber lasers use rare-earth-doped optical fibers for high optical gain. They can achieve high output power, even in the multikilowatt range, particularly in continuous-wave mode. Mode-locked Yb-doped fiber lasers produce ultrashort pulses in the picosecond or femtosecond range within a spectral range of 1020 to 1070 nm, with high pulse repetition rates. These lasers can reach peak powers in the megawatt range.

Ultrashort pulse durations reduce the Heat-Affected Zone (HAZ) in LIG fabrication and enable subdiffraction-limit patterning resolution. The HAZ is defined as the area, on the polymide, corresponding to a temperature increase that does not necessarily correspond to the spot size of the laser. High peak power fiber lasers are valuable for creating intricate patterns in LIG. The drawback is the high cost of this technology.

 CO_2 Long-Pulsed Lasers, with their long wavelength (10.6 μ m) and pulse duration (tens of μ s), are used to irradiate aromatic polymers and lignocellulose materials [16], resulting in the formation of multilayer graphene nanostructures. The laser's intense localized heating breaks the C-O, C=O, and N-C chemical bonds in the material, releasing gases and causing rearrangement of aromatic compounds, leading to the formation of graphene structures through laser-induced reactions.

Ultrashort-Pulsed Lasers are used to create LIG. [16] This process involves three steps: (1) Carbonization, where laser energy heats and converts the material into amorphous carbon; (2) Graphitization, where high temperatures (≈ 3000 K) transform amorphous carbon into structured graphene; (3) Exfoliation, where ultrashort laser pulses detach individual graphene layers from the surface. FsLIG requires lower power than CO₂ lasers and yields similar sheet resistance, making it useful in various applications, despite potential nonlinear interactions with the carbon precursor material.

LIG - Applications and Future Trends

This thesis investigates the Energy Storage potential of LIG as substrate for electrodes for μ SCs. These components require specific properties like high conductivity, flexibility, and stability. LIG provides porous, highly crystalline electrodes with a large surface area. Unlike traditional methods [14, 16], LIG fabrication eliminates the need for binders and conductive agents, simplifying production. It is not the only one research fields of interest [16] in which LIG is employed:

- **Biosensors.** It is well-suited for biosensing due to its large surface area, high electron density, and optical transparency. LIG biosensors consist of a receptor layer for specific binding to analytes and a transducing layer (LIG) to convert these interactions into measurable parameters. They are used for detecting enzymes, DNA/RNA, and immunosensing, with a focus on point-of-care and early disease detection, promising improvements in patient care.
- Physical Sensors. Graphene sensors are becoming vital for real-time monitoring in various advanced applications, including robotics, e-skin, healthcare, and IoT. They offer exceptional sensitivity, wide detection capabilities, quick responses, durability, and stability due to graphene's unique properties, making them a leading choice for modern sensing technologies.
- Photodetectors. They play a critical role in a wide array of applications, spanning from optical communications and spectrometers to fluorescence microscopes. Traditional photodetectors are bulky, fragile, and expensive, making them unsuitable for portable applications like wearables, where compactness, durability, and cost-effectiveness are crucial. Zhang et al. [16] created flexible ZnS/SnO₂ UV photodetectors by depositing nanoparticles on a polyimide sheet to be converted into conductive graphene through CO₂ Laser, leaving the rest as the sensing material. This photodetector had a high photodark current ratio, fast rise and decay times.
- Gas Sensors. LIG-based sensors hold significant potential in detecting various gases and providing crucial environmental information. To enhance sensitivity, the design incorporated LIG filaments. This configuration allowed the gas sensor to detect and distinguish between different ambient gases, including CO₂, N₂, O₂, and Ar.

This technology is poised to serve a wide range of purposes and applications in the near future, demonstrating its versatility and potential. [16] Integrated systems combining LIG components like sensors, supercapacitors (SCs), and triboelectric nanogenerators (TENGs) are likely to create portable and wearable electronics in a single manufacturing step. Research on LIG is evolving rapidly, with significant potential for exploring new materials and applications. The transition from lab research to commercial products is becoming increasingly likely in recent years, highlighting the promising future of LIG.

 μSCs



Politecnico di Torino

1.3.2 TMOs - Transition Metal Oxides

This research also focuses on Transition Metal Oxides (TMOs), a diverse group of materials with varying structures and properties. The unique characteristics of TMOs result from the behavior of their outer d-electrons, leading to a wide range of bonding interactions between metals and oxygen in these compounds.

What's particularly fascinating is the wide spectrum of electronic and magnetic properties [31] displayed by these oxides:

- On one end, we observe oxides with metallic traits (e.g., RuO₂, ReO₃, LaNiO₃), while on the other, there are oxides with strong insulating properties (e.g., BaTiO₃). Some oxides transition between these states with changes in factors like temperature, pressure, or composition (e.g., V₂O₃, La_{1-x}Sr_xVO₃). Additionally, interesting *electronic properties* emerge from phenomena like charge density waves (e.g., K_{0.3}MoO₃), charge ordering (e.g., Fe₃O₄), and defect ordering (e.g., Ca₂Mn₂O₅, Ca₂Fe₂O₅).
- Transition metal oxides also exhibit a wide range of magnetic properties, spanning from ferromagnetism (e.g., CrO₂, La_{0.5}Sr_{0.5}MnO₃) to antiferromagnetism (e.g., NiO, LaCrO₃). Many of these oxides can switch between different orientation states, seen in ferroelectric (e.g., BaTiO₃, KNbO₃) and ferroelastic (e.g., Gd₂Mo₂O₇) materials.

The most groundbreaking discovery in the field of solid-state science has undoubtedly been the observation of high-temperature superconductivity in cuprates. [31, 13]

TMOs - Physical and Chemical Properties

Outer electrons in solids are described using two main theories: Band Theory for s and p electrons with strong interactions and small energy differences, and Ligand-Field Theory for f electrons with effective shielding and large energy differences. Outer d electrons in transition metal oxides (TMOs) exhibit an intermediate behavior, displaying both itinerant and localized electron properties. [31] So, they possess distinct properties that set them apart from metallic elements, alloys, covalent semiconductors, and ionic insulators that arise from various factors:

- Oxides of d-block transition elements exhibit narrow electronic bands because of the limited overlap between the metal d and oxygen d orbitals. These band widths are usually on the order of 1 to 2 eV.
- Electron correlation effects play an important role, as expected because of the narrow electronic bands.
- Many transition metal oxides are not truly 3D, but have low-dimensional features.



 The polarizability of oxygen plays a significant role. While the divalent oxide ion (O²⁻) is a common description of oxygen, it doesn't fully represent its state, particularly in solid materials. Additional configurations, such as O¹⁻, become important, leading to polaronic and bipolaronic effects. A polaron is a quasiparticle used to understand the interactions between electrons and atoms within a solid.

The diverse characteristics exhibited by individual oxides have made it challenging to develop comprehensive theoretical models for complex transition metal oxides.

Thin Films Configuration

Two dimensional TMOs, called *Planar TMOs* or *2D-TMOs*, are known to show different characteristics with respect to their bulk counterpart. [13] They can exist as single layer, multi layer of the same TMO or multi layer of different TMOs: superlattices.

The special properties of these materials is due to the polarizability of O^{2-} that enables large, non-linear and non uniform distribution of charges within the lattice. As a consequence, exceptional interfacial properties will be generated due to the electrostatic screening. This phenomenon leads to the formation of energy states on the surface of planar transition metal oxides that differ markedly from their properties in bulk. Additionally, it fosters a strong attraction of 2D TMOs towards coulombic interactions with neighboring ions.

TMOs offer versatility with various metals. Cationic species and their oxidation state flexibility drive TMO properties. In 2D-TMOs, different charge states lead to diverse electronic behavior, including metal-insulator transitions. These materials have tunable bandgaps, enabling engineering of optical and electrical properties. Nanostructured TMOs show reversible redox properties, and many 2D TMOs exhibit strong chemical and thermal stability.

2D-TMOs Species. Depending on their crystal structure, several TMOs with different properties can be found: [13]

- Certain TMOs $(MoO_3, WO_3, ...)$ can exist naturally as layered crystals in hydrate or anhydrate phases. These oxides can be exfoliated into nanosheets with oxygen-terminated basal surfaces using liquid or gas-phase methods. Importantly, these nanosheets maintain stability in both air and water.
- Numerous other oxides, like sub-stoichiometric titanium and zinc oxides, lack a natural layered crystal phase. In such instances, they are typically exfoliated from their more stable stratified compounds or alternatively deposited using layer-by-layer methods. It's crucial to ensure the stability of these structures after growth, often achieved through charged motifs or functional groups.

- Perovskites represent a significant family of 2D TMOs, characterized by a general formula, ABO_3 . In this structure, A-site ions occupy the corners of the cubic unit cell, while B-site ions consist of transition metal elements at the center of the cubic unit cell. These materials can be directly synthesized into a 2D form using layer-by-layer deposition techniques, often followed by stabilization steps. Layered perovskites are composed of ABO_3 layers separated by thin sheets containing motifs with A and B cations, which may have varying sizes. Their properties can vary depending on the thickness of the motif layers and lateral alignment of the perovskite layers in relation to each other.
- Oxides sandwiched between insulators and metals, like planar cuprates and CoO_2 , are typically regarded as quasi-2D TMOs. Because electrons can move freely within these loosely coupled oxide layers, these materials may exhibit superconducting properties.

Synthesis Approaches. In general, mechanical methods or processes based on gas and liquid phases are used. [13]

- *Mechanical exfoliation* is a cost-effective and successful method for obtaining high-quality 2D TMOs from layered crystals, despite its low material yield and sporadic substrate coverage.
- In gas-phase processes, 2D film growth follows the *Frank-van der Merwe growth*, where planar crystal growth occurs when the substrate aligns with the 2D oxide layer. Factors like adatom flux and substrate surface energy influence the growth of TMOs. Progress in gaseous-phase physical deposition enables precise growth control at the unit-cell level using real-time reflection high-energy electron diffraction (*RHEED*) monitoring. Common vapor-phase techniques for 2D TMOs include *MBE*, *PLD*, *ALD*, and *CVD*. Accurate parameter tuning, including carrier gas, temperature, and power, is essential for depositing atomically thin oxide layers or superlattices.
- Oxide epilayers can be grown through *solvothermal processes* using hot liquid solutions, with or without directing agents. The solvent can vary, and a pressurized vessel may be needed depending on the solution's evaporation temperature. Different methods, like *Self-Assembly* and *Langmuir-Blodgett* techniques, can be used at room temperature in a standard laboratory environment. The purity of analytes and solvents can have a significant impact on the results. Electroplating is a *Solution-based techniques* that offer a one-step process for layer formation on a substrate. They are similar to vapor-phase deposition, maintaining proper unit cell alignment is important for effective charge carrier movement and exchange in these techniques. Control at the unit-cell level is essential for crystal alignments.



Politecnico di Torino

TMOs - Applications

The energy storage capabilities of TMOs as electrodes in μ SCs will be investigated within this thesis work. These materials offer several advantages [13] in this context, such as: (a) Ion storage capability: 2D TMOs have a natural ability to accommodate charged ions on their surfaces without mixing, making them ideal for ion storage; (b) High conductivity; (c) Large surface area: 2D TMOs possess extraordinarily large surface areas, enhancing the opportunities for electrochemical reactions and interactions with charges; (d) Electrochemical stability within their operational voltage windows, ensuring long-term reliability; (e) Fast ion kinetics: 2D TMOs exhibit relatively rapid intercalation and de-intercalation kinetics, enabling quick charge and discharge processes; (f) Planar geometry: their planar nanosheet structure is well-suited for planar device design, allowing for compact and efficient energy storage device configurations; (g) Expansion tolerance: these materials can undergo a certain degree of expansion without cracking, enhancing their durability during charge-discharge cycles.

TMOs possess distinctive properties due to the presence of oxygen and other characteristics, such as their tunability, dopability, and intercalation capabilities. These unique attributes enable a range of specialized applications: [13]

- Transition metal oxides (TMOs) have found extensive applications in **Electronics**. TMOs are used in electronics as high-k in FETs dielectrics, semiconductors, and even superconductors, enabling various devices, including transistors and memory components as resistive memories/memristors due to their excellent ferroelectric properties.
- 2D-TMOs can exhibit **Ferroic** behavior. This means they may demonstrate a hysteric response to an external stimulus, which can be attributed to their ferroelectric, ferromagnetic, or in some cases, both (as in multiferroics) properties. These ferroic characteristics play a significant role in the unique behavior and potential applications of 2D TMOs. Due to these unique properties, 2D-TMOs can be used in spintronics, for ferroelectric devices and ferromagnetic units.
- Thermoelectric applications of TMOs have been shown infour major categories of: cooling, energy scavenging, sensors and thermopower wave sources.
- 2D-TMOs possess high **Mechanical strength**, serving roles in reinforcing polymers and constructing 2D mechanical structures. They can also display piezoelectric behavior, converting mechanical stress into electrical signals.

Materials of interest

The aim of this work is to design and fabricate an asymmetric μ SC. So, anode and cathode will be decorated with two different TMOs:

Manganese Oxide. Due to its high capacitance, cost-effectiveness, and ecofriendly nature, it is a promising choice as electrode material in SCs. Efforts focus on nanostructured materials to boost surface area and enhance performance. However, the low conductivity of manganese oxide ($\sim 10^{-6} \text{ Scm}^{-1}$) limits its practical application in terms of specific capacitance and charge/discharge rates [45, 26].To address this limitation, a promising approach involves depositing a thin manganese oxide layer on the surface of a porous, high surface area, and electronically conducting structure, such as activated carbons (AC), carbon nanotubes (CNTs), carbon nanofibers (CNFs) and graphenes [26], maximizing manganese oxide utilization. Furthermore, current collectors like nanoporous gold (NPG) and nickel foam, with 3D nanoarchitecture, are ideal for manganese oxidebased hybrid electrodes. NPG, known for its high surface area, low density, and great conductivity, serves as a scaffold for depositing nanostructured manganese oxide materials. This improves their electrical and ionic conductivity, enhancing pseudocapacitive behavior.

Chen et al. achieved a remarkable specific capacitance of 1145 Fg^{-1} by electrolessly plating manganese oxide onto nanoporous gold [45]. This innovative hybrid structure facilitates rapid electron transport and ion diffusion, generating significant interest in developing high-performance hybrid electrodes with manganese oxide on nanoporous conductive architectures for advanced supercapacitors, thanks to their superior ion and electron kinetics compared to conventional electrodes. Commonly [15, 8, 39], nanoparticles are added to support substrates like carbon black or nanoporous gold, enhancing the performance of supercapacitor materials. Tang et al. modified nickel foam with Pt nanoparticles to create 3D manganese dioxide/Pt/nickel foam hybrid electrodes [45] with a maximum specific capacitance of 1222 Fg^{-1} at 5 Ag^{-1} . Similarly, Xia et al. introduced a thin layer of Pt nanoparticles on Co₃O₄ nanowires, resulting in hierarchical Co₃O₄@Pt@MnO₂ nanowire arrays with excellent supercapacitor performance.

A hybrid electrode combining nanoscale MnO₂ with porous carbon offers improved surface area, electrical conductivity and promotes uniform electrochemical reactions, reduced ionic resistance, and increase of both power and energy densities. [26] For instance, Zhang et al. synthesized highly porous honeycomb MnO₂@carbon fibers (HMO@CFs) using a hydrothermal method. This core-shell electrode exhibited a high capacitance of 295 Fg⁻¹ at a current density of 0.1 Ag⁻¹. Zhu et al. grew MnO₂ nanosheets in situ on activated carbon fibers (MnO₂/ACFs) through a microwave-assisted hydrothermal process, achieving a remarkable capacitance of 117 Fg⁻¹ at 10 mA cm⁻². Youe et al. prepared amorphous β/δ -MnO₂ crystals on lignin-derived carbon nanofiber mats (MnO₂/CNFMs) through hydrothermal decomposition, resulting in an electrode with a high specific capacitance of 171.6 Fg⁻¹ at a scan rate of 5 mVs⁻¹, which was more than six times that of CNFM. Politecnico di Torino

Iron Oxide. Iron is known as the fourth most abundant element on earth. The oxide form of iron is known to exist in 16 different phases. Among them, hematite $(\alpha$ -Fe₂O₃), maghemite $(\delta$ -Fe₂O₃), and magnetite (Fe₃O₄) are by far the most widely studied, but it also has interesting properties as a hydroxide (α -FeOOH, α/δ -FeOOH) [36, 21]. Iron Oxide has garnered attention as a cost-effective catalyst for the oxygen reduction reaction (ORR). Researchers have explored carbon-supported (graphene/graphene oxides GO) iron oxides and oxyhydroxides as potential ORR catalysts. However, there is limited understanding of how the type of iron species and their crystalline phases influence ORR activity.

Regarding the Energy Storage field, Lithium-Ion Batteries (LIBs) are prominent candidates for efficient systems due to their widespread applications. However, the current commercial graphite anode in LIBs has limitations, including a relatively low theoretical capacity of 372 mAh g⁻¹. To address this, researchers have proposed the use of electrochemically active materials in LIBs. Poizot et al. reported [23] that TMOs represent an important class of anode materials for LIBs, offering significantly higher theoretical capacities, approximately 2/3 times that of graphite. As a result, TMOs and related composites have garnered significant attention as potential anodes for LIBs. Iron oxide-based anodes in lithium-ion batteries face two main challenges: irreversible capacity caused by electrolyte decomposition and SEI formation during the first discharge, and the thermodynamically unfavorable extraction of Li⁺ from Li₂O, leading to partial irreversible capacity; second, these anodes suffer from poor cycling stability due to substantial volume changes and Fe aggregation during Li⁺ insertion and extraction, leading to electrode pulverization and capacity decay over time.

To address the challenges one highly effective strategy [23] is the *nanostructuring* of iron oxides. They offer several advantages: inhibiting the strain and volume variation that occurs during the insertion and deinsertion of lithium ions (Li⁺), leading to improved stability. Additionally, nanostructures enable easier diffusion of Li⁺ within the electrodes, promoting better electrochemical performance. Another important strategy [23] involves introducing *carbonaceous materials*, such as carbon fibers (CFs), carbon nanotubes (CNTs), graphene, and pyrolyzed carbon, to composite with iron oxides. These carbonaceous materials have unique structures that can buffer the volume variation of composite electrodes during charge/discharge, improving electronic contact and cycling stability of iron oxide nanostructures. Overall, the combination of nanostructuring and compositing with carbonaceous materials offers a promising approach to overcome the challenges associated with iron oxide-based anodes in LIBs.

In this work, Iron Oxide will be deposited onto LIG to act as a negative electrode for a μ SC.

Chapter 2

Methods - Fabrication Processes, Experimental Setups and Characterization Techniques

2.1 Direct Laser Writing Procedure

The schematic of the Laser Writing process to obtain LIG starting from a carbon precursor substrate is reported in Fig.2.1(a).



Figure 2.1: DLW System. (a) Schematic of DLW Process and equipment [14]. (b) CO₂ Laser. (c) DLW process

A polyimide called Kapton $C_{22}H_{10}O_5N_2$ has been used as carbon precursor in this work. It is characterized by several interesting properties, such as resistance to high temperatures, quite constant dielectric properties over a wide range of temperatures.

A CO_2 long-pulsed Laser depicted in Fig.2.1(b) was used during this work. This equipment is composed by the chamber where the laser irradiation will take place,

that is closed during the process to shield the outside from radiation and the internal extractor helps to remove the fumes produced, and by a monitor equipped with software to draw simple geometries or to import more complex ones, to be transferred to the kapton film. Before starting the process it is important to clean its surface with ethanol and to fix the kapton well stretched on the sample holder to minimize any folds during irradiation as shown in Fig.2.1(c), that may affect the resolution of the final geometry and the LIG's quality at the border.

In order to obtain LIG from this carbon precursor, it is important to know the parameters of the Laser that will irradiate it.

Laser Parameters. The physical and chemical properties of the obtained LIG are influenced by the Laser Parameters: [16]

- Power. One of the main Laser parameter is the power of its beam, expressed in Watts [W]. For pulsed laser it refers to the average value. Its selection, as usual, depends on the carbon precursor and the desired LIG properties. In particular, depending on the DLW system, a certain threshold exixts and must be overcome in order to fabricate LIG. Typically, below this threshold, the obtained material still remain an insulator. This property can be investigated by measurements of the sheet resistance: below the threshold it is very high ($\approx M\Omega \ sq^{-1}$); above the threshold it become very small ($\approx \Omega \ sq^{-1}$) and, by increase of the it, the sheet sesistance reaches a minimum. Further increase of the Laser power after ones the minimum has been achieved results in the degradation of the LIG due to its oxidation. To determine the threshold for LIG formation, it's more accurate to use Laser *Intensity* [W cm⁻²] or *Fluence* [J cm⁻²] when using pulsed lasers, since it depends on the beam spot size. These parameters provide better insights into the energy delivered to the material surface during the laser process.
- *Wavelength*. During the LIG formation a fraction of the laser energy is absorbed and converted into thermal energy, while the remaining fraction is reflected/scattered.

The absorption strongly depends on the wavelength of the incident radiation. Depending on this parameter, Lasers can be classified into UV (< 400 nm), visible (400 - 750 nm), near-infrared (NIR, 0.74 - 2.5 μ m) and mid-infrared (MIR, 2.5 - 25 μ m). Short Wavelength Lasers (< 390 nm) can dirctly break the covalent bonds between C atoms in athermal photochemical processes due to the high photon energy.

So, the selection of the wavelength, and consequently of the Laser, depends on the carbon precursor that will be use to produce LIG.

• Laser types vary by *Pulse Duration*: continuous-wave (CW), long-pulsed, and ultrashort-pulsed. Shorter pulses, as seen in ultrashort-pulsed lasers, provide higher peak power and quicker temperature rise. Shorter pulses also result in smaller Heat-Affected Zones (HAZ), enhancing spatial resolution. HAZ size

Politecnico di Torino Politecnico di Torino

is proportional to the square root of pulse duration. Therefore, ultrashortpulsed lasers offer precision and high-resolution material processing, including LIG fabrication.

- *Repetition Rate.* It refers to how quickly pulses are emitted, and it is vital for LIG fabrication. It must strike a balance to allow materials to cool effectively. Selecting the wrong rate can lead to problems like ablation or wide Heat-Affected Zones (HAZ). It depends on the material and laser properties, so finding the right repetition rate is crucial for quality LIG.
- Scanning Speed. The advantage of the DLW is that it is possible to obtain a certain pattern without using masks. So, a scan over the carbon precursor surface will be done. The Scanning Speed is inversely proportional to the exposure time of a given point to the beam. So, a high scanning speed generates a low temperature on the exposed area, and as a consequence, the resulting LIG will be characterized by a poor degree of graphenization and poor conductivity. On the other hand, a low scanning speed produces overheating on the irradiated spot, and so, defects on LIG or damages of the substrate.





2.2 Electroplating

This process is also known as Electrodeposition or Galvanic Deposition and it is the oldest technology in semiconductor industry. It consists in a bath containing the metal ions related to the material we want to deposit, an electrode over which there is the substrate and a power supply.

This process is characterized by a high deposition rate, up to some $\mu m \min^{-1}$.

By applying a current, a flux of the ions will generate within the bath. In particular, cations will move from the anode to the cathode and viceversa, anions will move in the opposite direction to close the circuit. The species will reduce at the cathode and so, there is a transfer of electrons from the electrode to the Ion, while they will oxidize at the anode.

The circuit must be closed in order to have a current different from zero, and so, the substrate must be conductive. In general, the growth of the film will be not only on the top of the substrate, but also on its lateral walls.



Figure 2.2: Cross Section of the steps of the Electroplating Process (for the TMO we want to deposit)

The steps of the process are reported in Fig.2.2. In this case, the conductive substrate is the LIG and the bath is the electroplating solution that will be described later.

The electrochemical approach is preferred with respect to other deposition processes since its reactors does not require high temperatures and collateral services. In this way we obtain environmental protection and pollution monitoring by using non-polluting energy sources. [37]



Experimental Setup

These experiments were done within a becher (reactor) containing: (1) the electroplating solution, (2) the working electrode WE that is LIG, over which we want to deposit the metal oxide, (3) the counter electrode CE (Platinum Pt) and (4) the reference electrode RE. All of them are connected to the *BioLogic*: the instrument to perform the technique.

The LIG electrode was attached to the beacher walls by menas of a kapton tape, as evidenced in Fig.2.3(a) and evaporation of the solution is avoided by closing the cell with a parafilm. Titanium (Ti) grid is used as electrical connection for the WE.



Figure 2.3: Electroplating experimental setup: (a) working electrode within the becher. (b) Vial cell cap

The cap in Fig.2.3(b) has been used for this process since its holes perfectly fit the entrance of the reference electrode and of the counter electrode.

Reference Electrode. The advantage of the Half Cell mode is the fact that the potential of the reference electrode is stable in the electrolyte solution and above all it does not polarize and variations in potential can be attributed to it. So, all the potential energy provided to the cell is applied only to the WE. All the characterizations will be performed in Half Cell mode, by exploiting a Ag/AgCl reference electrode.

The electrode works in a reversible redox reaction at equilibrium is between the solid Ag metal and its solid salt AgCl in a 3 M chloride electrolyte solution (NaCl in our case) contained in a glass tube with an aperture in the lower part characterized by a porous septum that allows diffusion (as shown in Fig.2.4(a)).

$$AgCl_{(s)} + e^{-} \rightleftharpoons Ag_{(s)} + Cl^{-}_{(aq)}$$

$$\tag{2.1}$$

CHAPTER 2. METHODS





Figure 2.4: Reference Electrode: (a) Ag/AgCl RE. (b) 3 M NaCl solution

Eq.2.1 describes the equilibrium redox reaction that occurs within the glass tube. By using the Nerst Equation, to this reaction it is possible to associate a standard reduction potential with respect to NHE.

So, the solution must be regenerated periodically in order to ensure the correct operation of the electrode.

Pt Counter Electrode. The growing interest in electrocatalytic reactions for energy-related applications has attracted researchers from diverse backgrounds. To assist these researchers, the electrochemistry community is developing guidelines and best practices for electrocatalysis research. This contribution addresses a specific challenge related to the use of Pt materials as counter electrodes.

For accurate results, it's crucial to maintain a meticulously controlled measurement environment. This involves thorough cleaning of the electrochemical cell, using highly pure electrolyte solutions, and ensuring electrode materials and gases are of the highest purity. Even tiny impurities can impact the studied electrode process. [11]

Materials chosen for counter electrodes should possess specific properties, including high electronic conductivity, excellent mechanical strength, chemical stability across a wide potential range, high purity, and cost-effectiveness. These properties ensure efficient electron transfer, durability, reliable performance, and affordability, contributing to accurate electrochemical experiments.

Platinum possesses numerous attributes mentioned earlier and has been a longstanding choice as a counter-electrode material. Nevertheless, both gold and carbon also fulfill many of these selection criteria and are commonly used for constructing counter electrodes. It's worth noting that no material remains perfectly stable across a wide potential range and in aqueous electrolyte solutions with varying pH levels. Consequently, it is very important to carefully consider the gradual but inevitable degradation of counter-electrode materials when planning and conducting electrochemical experiments. This issue becomes particularly significant in highly acidic or alkaline environments, where these materials are known to degrade. [11]



Figure 2.5: Platinum Counter Electrode

The electroplating processes will last quite a short time, typically some minutes in this research work, so a Pt rod (Fig.2.5) is used as counter electrode.

In Fig.2.5, the lower part of the Pt rod appears darker and this is a sign that the deposition has taken place. The Pt rod was thoroughly cleaned by means of acidic solutions to avoid contaminations during successive experiments.

Electroplating Solution. Aqueous solutions was employed during this work. The solutes are weighed and immersed in the solvent, reaching a certain concentration. Their masses can be evaluated in the following way:

$$m[g] = C[M] \cdot V[L] \cdot MW[g/mol]$$
(2.2)

where C is the wanted concentration, V is the volume of the resulting solution and MW is the molecular weight. The measurement units for all these quantities are reported in the square brackets, and for what concern the concentration, it is important to remember that $[M] = [\frac{mol}{L}]$.
Final Cell and Parameter Setting

The electroplating cell is reported in the picture of Fig.2.6. It is ready to be connected to the instrument in order to start the technique.



Figure 2.6: Electroplating Cell

Mechanical arms are used to keep a high mechanical stability to the whole cell and to keep the platinum still in order to ensure that the distance between the WE and CE remain fixed during the entire process (Fig.2.7).



Figure 2.7: Electroplating Experimental Setup: (a) Electroplating Cell and connections. (b) Electroplating Cell - Schematic

The procedure is configured through the *EC-Lab* software provided by *BioLogic*, by selecting the technique and setting all the parameters.

A constant current will be applied between the CE and the WE. The correspondent procedure is in fact called CstC (Constant Current). Then, the instrument measures the potential of the WE with respect to the RE. The parameters to be set are described in Table 2.1.

Parameter [Unit]	Description	
Rest Time [sec]	It is a period t_R during which the potential of the working electrode is measured in open circuit condition and the result at the end of it will be the starting point for the following potential recording.	
Deposition Time [min]	It is the period of time t_{DEP} during which the deposition current is applied.	
Deposition Current [mA]	It is the current I_{DEP} to be applied between CE and WE. The current must be chosen by considering the current density \mathbf{J}_{DEP} [mA cm ⁻²] that we want to apply and the Active Area A [cm ²] over which the electroplating will take place. In fact, these quantities are related by the following equation:	
	$I_{DEP} = J_{DEP}A \tag{2.3}$	
	from which we can compute the Current I_{DEP} to be applied in order to obtain the desired Current Density.	
WE's Potential [V]	It is the quantity to be measured by the instrument during the period in which the Current is applied. In the plot it is indicated as <i>Potential vs.</i> $Ag/AgCl$	

Table 2.1: Electroplating - Parameters

Evaluation of the amount of deposited mass



Figure 2.8: Balance used for the mass evaluation

The mass of the electrodes have been measured with the balance of the KERN-ALJ series. Its resolution is 0.01 mg and it is equipped with equipment for wind protection and air ionization. A ceramic crucible, as shown in Fig.2.8, is employed to hold the sample on the sample holder. This approach increases the measured gross weight, allowing the instrument to operate in a higher range with improved resolution.

Since the amount of deposited material is very low by applying the electroplating process, a very precise measurement must be done. To this aim, the mass of each sample has been evaluated 10 times before the process and 10 times after it. It is important to highlight the fact that, during

the plating the samples are within the ds they are wet. They are left to dry in a

solution and so, immediately afterwards they are wet. They are left to dry in a desiccator for at least 4 hours before being weighed.

For each sample, the *Mean Value* and the *Standard Deviation* were computed by compiling a MATLAB script in the Appendix 4.3.

The two results can be expressed as:

- $\mathbf{m}_i = \mathbf{m}_{i_0} \pm \sigma_{m_i}$
- $\mathbf{m}_f = \mathbf{m}_{f_0} \pm \sigma_{m_f}$

where m_{i_0/f_0} are the mean values and $\sigma_{m_{i/f}}$ are the standard deviation. Once the mass of the electrode has been measured before (m_i) and after (m_f) the deposition process, the amount of deposited material can be estimated by computing their difference:

$$\Delta m = m_f - m_i \tag{2.4}$$

and the error is obtained by propagating the standard deviation in the following way:

$$\sigma_{\Delta m} = \sqrt{\sigma_{m_i}^2 + \sigma_{m_f}^2} \tag{2.5}$$

As for $m_{i/f}$, also this quantity will be declared in the same way:

• $\Delta m = \Delta m_0 \pm \sigma_{\Delta m}$

where Δm_0 is the mean value $(m_{f_0} - m_{i_0})$ and $\sigma_{\Delta m}$ is the standard deviation of the amount of deposited material.



Theoretically, the amount of mass deposited onto the LIG surface can be estimated through the Faraday's Law:

$$m_{th,TMO} = \frac{MW_{TMO} \ I\Delta t}{4nF} \tag{2.6}$$

where MW_{TMO} is the molecular weight of the compound to be deposited, F is the Faraday's constant (F $\simeq 96.485 \cdot 10^3$ C mol⁻¹), $I\Delta t$ is the amount of charge transferred on the surface and n is the number of electrons involved in the reaction. For example, in the MnO deposition case, we start from the Mn in the Manganese Acetate with Oxidation Number $n_{OX} = +2$ and we finish with the Mn atoms in the thin film layer onto the LIG surface with a different n_{OX} .

From this theoretical model, it is possible to evaluate the efficiency of the process as:

$$\eta_{DEP} = \frac{\Delta m}{m_{th,TMO}} \tag{2.7}$$



2.3 Material Characterization

2.3.1 FESEM

Scanning Electron Microscopy (SEM) is a physical characterization through which it is possible to observe the morphology of a surface at the nanoscale with higher resolution with respect to optical microscopy.

Physical Effect. The sample to be studied is impinged by an electron beam called primary beam characterized by some parameters that are important for the resolution of the final image. These electrons will interact with the surface and will reflected back in order to be detected. They can have the same energy of those coming from the beam or can lose some energy due to several scattering events within the first layers of the specimen. These electrons can be distinguish into 2 categories:

- Back Scattered Electrons (*BSE*). They possess the same energy as the electrons of the primary beam and they are reflected back through Coulomb repulsion.
- Secondary Electrons (SE). They lose their starting energy due to several collision with the electrons within the material. Their energy is typically around 50 eV. They are useful to obtain information about the volume of interaction within the sample.



Figure 2.9: Working principle of Scanning Electron Microscopy

Also other signals coming from the sample (as can be observed from Fig.2.9) can be studied in order to have more information.

The volume of interaction depends on the kinetic energy of the electrons of the primary beam and on the density of the material.

Experimental Setup. A typical FESEM equipment consists in:

- Source. It will generate the primary beam and so, it is also called Electron Gun. It can work by thermionic effect or by field emission and for this reason it is called *Field Effect SEM*: FESEM. In the first case the electrons are extracted from a Tungsten or Lanthanium Esabhorine filament. The second one is used to increase the electron extraction efficiency. The filament is biased in order to increase its temperature by Joule Effect. In the second case a very thin film of Tungsten is placed very close to an electrodes pair that will provide a high electrostatic field.
- Column. Here, the electrons of the primary beam will travel from their source to sample. Ultra High Vacuum is maintained in this environment to avoid contamination and increase the mean free path. Finally, the column is characterized by a system of electromagnetic condenser lenses that are able to deflect or focus the beam in order to reach the minimum possible spot size, typically 0.7-1 nm, and increase the resolution. At the end of the path in the column there will be the sample holder.
- *Detection System.* Depending on the type of electron, several detectors will be placed within the chamber. Typically a semiconductive one is used to measure BSEs, while a Everhart-Thornley detector is used for SEs.



Figure 2.10: FESEM equipment

The good quality of the SEM image will depend on some parameters of the primary beam: strength of the condenser lenses to focus the beam and improve the resolution, working distance WD to obtain the focus on the sample and accelerating voltage that will provide energy to the electrons of the beam.





2.3.2 XPS

This is a technique useful to obtain information about the occupied electronic states of a surface. Here, the sample surface will be irradiated by a UV or X-Ray beam, which photons will be absorbed by the atoms. They will release this excess of energy by emitting electrons called photoelectrons. They will be collected and their Energy Spectrum will be studied to obtain the knowledge of the chemical elements of the surface. Through this technique, also possible contamination could be detected. [22]

Physical Effect. This characterization method is based on the Photoelectric Effect. It should be treated by exploiting a quantum approach, but it can be simply described by a three step model: [22]

- Optical *Excitation* of an electron from an initial to a final state;
- *Propagation* of this electron through the material's surface, scattering off atoms. The mean free path is the distance between two successive scattering events. It depends on electron energy, typically from incident photons, and is material-independent. Scattering events cause the electron to lose energy information;
- *Emission* of the electron from the surface.

Experimental Setup. A typical XPS equipment [22] consists of:

- Light Beam Source.
 - X-Ray Tube. They emit photons due to electrons bombardment of an anode typically made of Mg or Al. The emission lines depend on the selected anode material.
 - Synchrotron Radiation. They provides a continuous spectrum of wavelength extending from far infrared to hard X-ray.
- Electron Energy Analyzer.
 - Hemispherical analysers are required for angle-resolved spectroscopy
 - Cylindrical mirror analyzer if angle resolution is not required
- Data Acquisition System. The obtained spectrum shows the intensity of the electron detector signal as a function of electron binding energy. It will be superimposed to a background noise signal due to the detected electrons after scattering events.



Figure 2.11: Schematic of a XPS equipment

The measurements are carried on in ultra high vacuum (UHV) in order to avoid contaminants adsorption on the surface to be studied, to increase the Mean Free Path of the emitted electrons and to prevent formation of discharges due to the ionization of the chamber atmosphere.



2.4 Electrochemical Characterization

The functionality of a supercapacitor can be assessed by a range of essential factors, such as:

• Cell Capacitance C

Politecnico di Torino

- Operating Voltage ΔV
- Equivalent Series Resistance ESR
- Coulombic Efficiency η_C
- Energy Efficiency η_E
- Energy Density E
- Time Constant τ

To precisely gauge these factors, numerous techniques have been suggested and are employed within academic and industrial domains.

An electrochemical characterization can be performed in two modes:

- Full Cell with two electrodes: a positive (WE) and a negative electrode (CE). In this case the measured voltage is the difference ΔV between the two electrodes.
- *Half Cell* with three electrodes: a working electrode (WE), counter electrode (CE) and reference electrode (RE). The techniques are applied by controlling the WE's potential and the potentials of the two electrodes are measured separately with respect to the RE.

The experiences that will be described in the following have been done in Half Cell mode. Typical characterizations that are used to evaluate the performances of a Supercapacitor electrodes are the Cyclic Voltammetry (CV) and the Electrochemical Impedence Spectroscopy (EIS). The output of all these measurements are voltages, currents and time, and from them it is possible to extract the parameters written before.

All of them starts after the measurement of the Open Circuit Voltage (OCV), which result is the steady state polarization level of the electrode in the solution with respect to Ag/AgCl. These electrochemical characterizations have been carried out with the VMP3 provided by *BioLogic*, by connecting the cell and set all the parameters for the stimulation of the cell through the *EC-Lab* software.

These are the most important ones, but also other techniques can be performed in order to evaluate other parameters or physical/chemical phenomenon.

2.4.1 Experimental Setup

Politecnico di Torino

All the experiments performed to obtain an electrochemical characterization for a single electrode will be done in Half Cell mode in a becher containing the aqueous electrolyte, the working electrode WE to be characterized, the counter electrode CE and the reference electrode RE (discussed in Section 2.2).



Figure 2.12: EC Characterization: experimental Setup. (a) Rectangular WE and circular CE; (b) Glass fiber separator; (c) Final setup

Ti grid is used as current collector for both the WE and CE depicted in Fig.2.12(a). It is important to underline the fact that, in order to obtain good and repeatable results, WE and CE were not left free to move in the electrolyte, but were pressed in front of each other by glass slides with rubber bands as shown in Fig.2.12(c) and glass fiber as separator between them in order to avoid short circuits, of thickness 675 μ m as shown in Fig.2.12(b).

Parafilm is used to properly seal the electrochemical cell, avoiding thus electrolyte drying. The final cell is reported in Fig.2.13.



Figure 2.13: Electrochemical Cell

AC Counter Electrodes. Active Carbon Electrodes are employed in systems with a limited amount of electrolyte where using Pt is not feasible. In such cases, it acts as a nearly non-polarizable counter electrode to avoid electrolysis. Additionally, it can serve as a pseudoreference electrode.

Oversizing counter electrodes assures the virtually non polarizable condition, or it limits the CE polarizability upon working electrode current flow. In *half cell* configuration, the applied voltage is it is adjusted only between WE and RE and therefore the capacity that is measured is that of the WE because the RE does not absorb current. The current generated by the WE flows into the CE which is made larger to prevent it from polarizing beyond the electrolysis limits and so, the only measured impedance is the one of the WE. In *full cell* mode instead, the cell equivalent capacitance to be considered, shown in Fig.2.14, is:

$$C_{eq} = \frac{C_{we}C_{AC}}{C_{we} + C_{AC}} \approx C_{we} \tag{2.8}$$

where C_{we} is the capacitance of the working electrode and C_{AC} is the one of the Active Carbon. The approximation holds if $C_{we} \ll C_{AC}$.



Figure 2.14: Equivalent Circuit of the electrochemical cell in full cell configuration

The fabrication process of these electrodes starts with the preparation of a solid material dispersion, which then dried until a ductile doughy state. It involves the addition of 3 g of active material in 50 mL of ethanol. It is made by three different components:

- 85% Active Carbon (AC): YP 50F. $m_{AC} = 2.55$ g
- 10% Carbon Black (CB): C65. $m_{CB} = 0.3$ g
- 5% PTFE solution: binder. $m_{PTFE} = \frac{0.15}{0.6}$ g = 0.25 g





Figure 2.15: Active Carbon CE fabrication steps: (a) Preparation of the dispersion. (b),(c) Solid state preparation. (d) Press. (e) Puncher to obtain circular shape. (f) Final result

Fig.2.15(a) shows the becher containing the solution. An aluminum paper covers the lower part to keep a uniform temperature at 60° C and avoid dissipation. After a few hours in these conditions, the preparation is ready to be handled with two spatulas and with the hands as reported in Fig.2.15(b), and by adding some ethanol if necessary, in order to provide it the wanted consistency obtained in the picture of Fig.2.15(c). In Fig.2.15(d) the press that was used to reach the desired thickness for the CEs is depicted. The slurry is sandwiched between plastic sheets in order to keep it uniform and to avoid possible contaminants on the surface of the press roller.

At this point circular shapes of 12 mm diameter are cut out using a puncher reported in Fig.2.15(e). A lot of electrodes were obtained through this fabrication process as can be seen from Fig.2.15(f).

2.4.2 EC Characterization Techniques

Open Circuit Voltage (OCV)

It is simply a measurement of the potential of the WE in open circuit condition: I = 0 A. This technique is set for a certain period of time of about a few hours to see a stable potential at the end of which the measured potential value indicated as E_{OC} or OCP: Open Circuit Potential. It is used as a reference point for the CV, in order to optimize the measurement to obtain a greater potential window and avoid power consumption.

Parameter [Unit]	Description
Rest Time [sec]	It is a period t_R during which the potential of the working electrode is measured in Open Circuit Condition and the result at the end of it will be the starting point for the following potential recording.
WE's Potential [V]	It is the quantity to be measured by the instrument during the t_R time, as E_{we} or $\langle E_{we} \rangle$: mean value.

Table 2.2: OCV - Parameters

The parameters setting can be done through the EC-Lab software and the main ones are explained in Table 2.2.

Electrochemical Impedance Spectroscopy (EIS)

During this analysis the cell is stimulated by sum of a steady-state voltage and a time dependent signal characterized by a certain frequency ω and typically low amplitude V_a :

$$V_{applied} = V_s + \Delta V(\omega). \tag{2.9}$$

where $V_{applied}$ is the voltage applied to the cell, V_s is the steady-state and $\Delta V(\omega)$ is the time dependent signal that can be expressed as a periodic function:

$$\Delta V(\omega) = V_a e^{i\omega t} \tag{2.10}$$

Parameter [Unit]	Description
WE's Potential [V]	It is the operating point of the stimuli.
Excitation Signal Mode	It corresponds to the type of periodic function to be applied in time in order to excite the cell. It can be <i>Single Sine</i> or <i>Multi Sine</i> mode.
f_i, f_f [Hz]	They are the limits of the frequency range in which the signal is applied.
N _d	It is the number of points to be analyzed per frequency decade.
Va	It is the amplitude of the applied stimuli.

All the parameters regarding the applied signal are reported in Table 2.3.

Table 2.3: EIS - Parameters

The output of this excitation is the current flowing in the cell, which periodic part can be written as: $\Delta I(\omega) = I_{max}e^{i(\omega t+\phi)}$ (ϕ is a phase shift). The Impedance Z can be computed, from these quantity, by applying the Ohm's law, as:

$$Z(\omega) = \frac{\Delta V(\omega)}{\Delta I(\omega)} \tag{2.11}$$

The Impedance is a complex function of the frequency ω : $Z \in \mathbb{C}$. Depending on how it is mathematically expressed in Eq.2.12, one can obtain the *Bode Diagram* through magnitude and phase or the *Nyquist Plot* by exploiting the Real and Imaginary part.

$$Z(\omega) = Z'(\omega) + iZ''(\omega) = |Z|(\omega)e^{i\phi(\omega)}$$
(2.12)

In this equation, i is the imaginary unit, Z' and Z'' are the real and imaginary part, while |Z| and ϕ are magnitude and phase. All of them are frequency dependent quantities. [46, 35]

It is good practice to perform this characterization before and after the CV to observe how the Impedance of the cell changes after the applied cycles.



Figure 2.16: Equivalent circuit describing the physical phenomenon

Several equivalent circuits and models have been developed to separate each contribution to the total impedance due to all the individual structure component in a cell system.

A SC can be described as the series of: (1) a capacitance, due to the accumulation, at the electrode-electrolyte interface, of charges of the forming double layer and (2) a resistance, due to different contributions: the uncompensated resistance R_U due to the presence of ions in the electrolyte and the charge transfer R_{CT} across the electrode-electrolyte interface. The described equivalent circuit is schematized in Fig.2.16. [35]

In the most simplified model a SC can be seen as the series of its capacitance and the equivalent

series resistance, as depicted in Fig.2.17. By applying the Fourier Transform to this simple circuit, the total Impedence can be written as:

$$Z(\omega) = ESR + \frac{1}{i\omega C_{eq}} = ESR - i\frac{1}{\omega C_{eq}}$$
(2.13)

The overall resistive contribution is called Equivalent Series Resistance ESR, obtained from Eq.2.13 for $\omega \to \infty$.



Figure 2.17: Simplest Circuit Model for a SC

A very useful diagram that can be obtained from this analysis is the Nyquist Plot. Here, the real and the imaginary part are reported in a Complex Plane. For a real SC the electrodes can be described by a more complex and complete model should be considered. It is represented in Fig.2.18 with its corresponding Nyquist Plot. This equivalent circuit that includes the components described in Fig.2.16, where Q_i is a non ideal capacitance and Z_d represents the ion's diffusive behaviour due to pores impregnation. Here, the semicircle corresponds to the R//C group, its low intercept with the Z' axis is the ESR, the oblique line represents Z_d and the vertical line is the capacitance that is present due to EDL's charging.



Figure 2.18: Nyquist Plot for a Supercapacitor's electrode

Cyclic Voltammetry (CV)

During this analysis, a linear increasing voltage is applied between the working and the reference electrode in order to charge the SC, and it is followed by a linear decrease of the voltage to discharge it. This stimuli is applied for a certain number of times, named as cycles within this characterization, in order to see how the parameters extracted from the results of the process vary for each of them.

The very important parameters to set before starting the test are described in Table 2.4.

Parameter [Unit]	Description	
Scan Rate [mV s^{-1}]	It is identified by the symbol ν the slope of the linear potential increase.	
Potential Window [V]	It is the range of the applied voltage ΔV . It depends on the materials of the electrode and in particular on the electrolyte used in the cell. It can start from the E_{OC} or from Ref , while the higher point has to be selected, depending on the system.	
Number of Cycles	It is the number n_C of applied charge/discharge process imposed to the cell. It is important to evaluate the <i>Capacitance Retention</i> : the variation of the capacitance or other quantities at each charge/discharge cycle. In general, it is good for supercapacitors with respect to standard Capacitors.	

Table 2.4: CV - Parameters



Figure 2.19: CV signals and results

Fig.2.19(a) shows the potential applied to the WE with respect to the reference electrode, during just one cycle and for different Scan Rate within the same potential window ΔV . So, the charge phase starts from E_{OC} , indicated as E_i in Fig.2.19(a) and finishes at $E_{OC} + \Delta V$, indicated as E_1 in Fig.2.19(a), while the discharge phase starts from E_1 and finishes, with the same and opposite slope, at E_{OC} , that is E_2 in Fig.2.19(a).

The measured quantity is the current $\langle I \rangle$, as it can be seen from Fig.2.19(b).



((a)) Charge/Discharge, one cycle

((b)) Charge/Discharge, all cycles

Figure 2.20: Charge/Discharge

The constitutive equation for an ideal capacitor is:

$$i(t) = C \frac{dv(t)}{dt}$$
(2.14)

where $\frac{dv(t)}{dt}$ is the Scan Rate in case of triangular signal. So, as a result of such excitation one should obtain a positive constant current during the charge phase and a negative constant current during the discharge phase: a rectangle in the I-V

plot. Anyway, the real result is a more complex structure, due to the fact that nonidealities such as parasitic resistances, oxidation reactions at the electrolyte-active area interface, etc... must be taken into account and the equation 2.14 alone is not enough to describe the correct behavior of the current as a function of a voltage variation. As a consequence, the results coming from the CV characterizations will have a pseudorectangular [18] shape.

As an example, the red curves of Fig.2.19(a) and Fig.2.19(b) show the stimuli and the result of the Current $\langle I \rangle$ measurement for the last cycle of the cell stimulation at 1 mV s⁻¹. The parameters of the CV are indicated in the upper left part in the plot of Fig.2.19(b). From this plot it is possible to extract some important parameter to evaluate the cell performance:

• Cell Capacitance. It can be evaluated by exploiting the formula that relates the charge stored at the capacitor electrode to the applied voltage:

$$Q = CV \Leftrightarrow C = \frac{Q}{V} \tag{2.15}$$

It is equivalent to the Eq.2.14. The charge can be evaluated during the discharge phase as Q_{dis} , while the charge phase is characterized by several uncontrolled faradiac reactions at the interface between the active area and the electrolyte. During this phase the charge stored is named as Q_{ch} .

The Q_{dis} can be extracted from the measured current by exploiting the equation:

$$I(t) = \frac{dQ_{dis}}{dt} \Leftrightarrow Q_{dis} = \int_{t_i}^{t_f} I(t')dt'$$
(2.16)

where t_i is the time at which the discharge phase starts $(V = E_{OC} + \Delta V)$ and $t_f = t_i + \Delta t$ is the time at which it ends $(V = E_{OC})$. Δt is the duration of the discharge phase, and it depends on the Scan Rate. So, the cell capacitance can be computed as:

$$C = \frac{\int_{t_i}^{t_i + \Delta t} I(t') dt'}{\Delta V}$$
(2.17)

 $Q_{dis/ch}$ is also called **Discharge/Charge Cell Capacity**, and it is another parameter that characterize the cell that can be expressed in mAh.

• Coulombic Efficiency. It is defined as the ratio between the charge stored during the discharge phase and during the charge phase and it is important to evaluate the difference in these two mechanisms:

$$\eta_C = \frac{Q_{dis}}{Q_{ch}} \tag{2.18}$$

The Q_{ch} is higher than the Q_{dis} because of some reactions at the interface between the active area and the electrolyte, and so, this parameter is lower than 1. Anyway, for SC it can be very high, reaching also values very close to 1 in many cases.

Politecnico di Torino • Energy Efficiency. Similarly to the Coulombic Efficiency, it is defined as the ratio between the energy released during the discharge phase and the Energy stored during the charge phase:

$$\eta_E = \frac{E_{dis}}{E_{ch}} \tag{2.19}$$

The energy density E_j $(j = \{dis, ch\})$ can be obtained as the integral of the instant Power:

$$E = \int_{t_i}^{t_f} P_{ist}(t')dt' = \int_0^{\Delta t} V(t')I(t')dt'$$
(2.20)

where V is the voltage applied to the cell and I is the current flowing into the SC. $\Delta t = t_f - t_i$ is the time interval required, for the SC, to be charged or discharged.

As an alternative, once the Capacitance has been computed, the Energy can be written as:

$$E = \frac{1}{2}CV^2 = \frac{Q^2}{2C}$$
(2.21)

Eq.2.15 has been used to switch between the two expressions.

• **Time Constant**. It is the time required by the device to reach the 63% of its total charging capacity. It can be computed, once the capacitance and the equivalent series resistance are known, as:

$$\tau = RC \tag{2.22}$$

It could be interesting to observe the behaviour of the CV for each cycle and how the parameters varies. An example is reported in Fig.2.20(b), where it is possible to observe how, after a certain number of cycles, the CV plot stabilizes.

In particular, by increasing the number of cycles, the peak that can be observed at the end of the charge phase, that is related to the oxidation reactions at the interface between the active area and the electrolyte, became less evident.

The capacitance value usually decreases at each cycle and this behaviour is known as *Capacitance Retention* and can be evaluated as the ratio between the value at the first and at the last cycle. It is important to perform a very high number of cycles in order to assess electrochemical stability and gain insights into potential effects like activation or degradation, it's crucial to monitor how capacity retention evolves over time.

Regarding the scan rate, typically was chosen low, $\nu = 1 \text{ mV s}^{-1}$, to have a more reliable idea of the electrochemical stability and to try to increase the potential window; it was increased, up to $\nu = 10 \text{ mV s}^{-1}$, to make quick comparisons. Another important observation is the fact that the CV plot will be different by considering different Scan Rates, and so, also the corresponding extracted parameters will be different, as shown in Fig.2.19(b). The capacitance should be, in general, inversely proportional to the Scan Rate ν .





2.5 Device - Electrochemical Charcterizations

Once the devices have been synthesized through Laser Writing and electroplating, they are ready to be characterized. To this aim they were mounted in *Pouch Cell* configuration.

2.5.1 Pouch Cell

The device, composed by Kapton substrate, LIG-MnO | LIG-FeO, is attached to a glass slide. A diamond tip is used to cut the sides of the glass slides and to obtain the desired dimension and shape.

Active Carbon electrodes are used as pseudo reference electrode and another Titanium strip was cut to act as an electrical contact for it. Then, a piece of fiberglass used as separator is placed on the device to avoid short circuits with the RE and, above all, to be wetted by the electrolyte. Then, another glass slide will close the system from above as can be seen from the images of Fig.2.21(a) and Fig.2.21(b).



Figure 2.21: Pouch Cell (c). Components and Steps for the Pouch Cell fabrication (a), (b)

A schematic of the Cross Section of the obtained system is reported in Fig.2.22. At this point the device can be sealed within Aluminum foil. Their size must be such as to allow the titanium contacts to come out. To prevent cuts or breakages, it is important to carefully file the edges of the slides before inserting the device inside these sheets. The welding on the sides where there are titanium contacts takes place by applying thermoplastic material which acts as a gasket, so these sides are welded flat. Before sealing the last side, the electrolyte is inserted within the cell by using a pipette and the vacuum is created.





Figure 2.22: Cross Section of the Experimental Setup for Device Characterization

The final result is shown in Fig.2.21(c). In this picture, the device is connected to the BioLogic channel to perform EC characterizations.



Figure 2.23: Schematic of the Pouch Cell (Cross Section)





Figure 2.24: Schematic of the Pouch Cell (Top View)

2.5.2 Electrochemical Characterization Techniques

Finally, in this section, a description of the techniques to electrochemically characterize a device will be done.

As for the single electrodes, devices have been characterized thorugh CV and EIS analysis in 2 electrodes configuration. Regarding the Voltammetry, it is important tu underline the fact that the applied potential window is the sum of the two potential windows applied on the two electrodes separately. The final device was optimized to work up to 1.9 V at 10 mVs^{-1} . For what concern the EIS, the total impedance is simply evaluated as the series of the impedances of the two electrodes.

Another technique that was used to charcterize the device is the GCD.

Galvanostatic Charge Discharge (GCD)

This technique is similar to the CV, but instead of controlling the pouch cell stimulus in voltage, it is controlled in current. Ideally, by applying a constant current and by inverting Eq.2.14, the voltage should increase or decrease linearly depending on the sign of the current.

The stimulation during a single cycle which duration is Δt can be expressed as:

$$i(t) = \begin{cases} I_C & t \in [0, \frac{\Delta t}{2}] \\ I_D & t \in [\frac{\Delta t}{2}, \Delta t] \end{cases}$$
(2.23)



Figure 2.25: GCD - Control Signal

where I_C charge the SC and I_D is negative and discharge the device as shown in Fig.2.25. The measured quantity is instead:

$$v(t) = \frac{1}{C} \int_{t_i}^{t_f} i(t') dt' = \frac{I_{C/D}t}{C}$$
(2.24)

As for the previously discussed characterizations, also for this technique it is important to properly set the parameters in Table 2.5.

Parameter [Unit]	Description
Current Rate [µA]	It is the charge or discharge current applied to excite the device. It is important to investigate several rates and to perform several cycle for each of them. $I_{C/D}$ don't necessarily have to be the same.
$V_{MIN}, V_{MAX} [V]$	They are the extremes that must not be exceeded by the measured voltage.
Cycle Time [s]	It is the duration of a single cycle, composed by the charge and discharge phase.
Number of Cycles	It is the number \mathbf{n}_C of applied charge/discharge process imposed to the device.

Table 2.5: GCD - Parameters

The measured voltage described by the Eq.2.24 should be ideally a triangular function of time comprised between the two voltages reached during the charge and discharge phase: V_{MAX} and V_{MIN} . Anyway, for a real device, the linear trend is distorted due to all the parasitic elements present in the measurement cell and in

particular the ESR causes a voltage drop between the end of the charging phase and the beginning of the discharge one (or viceversa).

From the measurements of this characterization it is possible to obtain some important plots and information:

- Ragone Plot. It is a chart used for the comparison of the performance of various energy-storing devices where the values of energy density (in Wh kg⁻¹ or Wh cm⁻²) are plotted vs power density (in W kg⁻¹ or W cm⁻²). ESDs such as batteries, capacitors, supercapacitors, flywheels, magnetic energy storage devices, etc., are located in characteristic regions in the power/energy plane in the Ragone plot. Both axes are usually presented in logarithmic scale, which allows the comparison of the performance of very different devices.
- The capacitance and the others obtained quantities can be evaluated as a function of the cycles, obtaining information about *Rate Capability*, *Cyclability*, that is high in SCs, up to a few tens of thousands of cycles, and *Accelerated Aging*.

Chapter 3

Results

3.1 Single Electrode Fabrication & Characterization

In this chapter the two electrodes of the final expected device will be studied separately, in order to optimize each of them individually, and only after this analysis they will be put together.

The first task is to obtain the LIG substrates for the following TMOs deposition through DLW. The following parameters have been used for the process in raster fill mode:

- Power: 19%
- Frequency: 5 kHz
- Resolution: 400 dpi
- Scan Speed: 375 mm s^{-1}
- Pulse Duration: 14 μ s (delay between two following pulses)



Figure 3.1: LIG electrodes



The output of the Laser Writing process is reported in Fig.3.1(a). It is possible to observe the goodness of this technique in terms of speed, as it is possible to obtain numerous electrodes in a single step, while Fig.3.1(b) shows one electrode after cutting it from the surrounding other electrodes and excess kapton to be easily used for the following treatments: TMOs electroplating and preparation for characterizations. Their lateral thickness is 1 cm.

3.1.1 MnO Electrode - Anode

Electroplating

The technique has been explained in Section 2.2. Here, the data, in terms of solution preparation, parameters selection and results analysis will be discussed.

Solution Preparation. The first task is the preparation of the solution containing the Mn atoms and support salt. The solution was composed by:

- 0.1 M, Manganese Acetate: $Mn(CO_2CH_3)_2$, MW = 173.03 g mol⁻¹
- Support Salt. For this process, three sulfates X_2SO_4 in concentration 0.1 M were used, varying the size of the ion X⁺ reported in Table 3.1 (Li⁺, Na⁺ and K⁺, belonging to the group of alkali metals) dissolved in solution. The hypothesis on which this experiment is based is that, by varying the ionic radius of the supporting salt, the layer-by-layer growth mode of the Metal Oxide also varies, acting as *interstitial doping* and increasing the space between two successive layers. The consequences on capacitive performances will be discussed later.









 $((c)) K_2 SO_4$

Figure 3.2: Sulfates X_2SO_4 used as Support Salts

((b)) Na₂SO₄

CHAPTER 3. RESULTS			
$\mathbf{MW} \; [\mathbf{g} \; \mathbf{mol}^{-1}]$	Cation	Ionic Radius [pm]	
109.94 142.04 174.26	$\mathrm{Li^{+}}_{\mathrm{Na^{+}}}$	182 227 280	
	CHAPTER 3 MW [g mol ⁻¹] 109.94 142.04 174.26	CHAPTER 3. RESULTS MW [g mol ⁻¹] Cation 109.94 Li ⁺ 142.04 Na ⁺ 174.26 K ⁺	

Table 3.1: Support Salt parameters

Eq.2.2 can be used to compute the masses to be measured for the Manganese Acetate and the Sulfates reported in Fig.3.2, in order to obtain the final solution of volume V:

- $m_{Mn(CO_2CH_3)_2} = 0.1 \ \frac{mol}{L} \cdot V \cdot 173.03 \ \frac{g}{mol}$
- $m_{X_2SO_4} = 0.1 \; rac{mol}{L} \cdot \mathrm{V} \cdot \mathrm{MW}_X$

where MW_X can be seen from Table 3.1. The solution is mixed by immersing a magnet in it and by switching on a magnetic field through the plate in Fig.3.3(a).



Figure 3.3: Electroplating Solution

It is important to underline the fact that this solution precipitate very quickly and so, before each deposition it must be mixed.

Deposition Process. The LIG electrodes are prepared for the deposition process and for the following electrochemical characterization by connecting it to the usual Ti grid as current collector as shown in Fig.3.4. Three samples have been synthesized for each Support Salt and so, they were labeled as $S_{i,j}$, where S stand for sample, the index i explains which of the 3 samples we are considering $(i = \{1, 2, 3\})$ and j describes the deposited oxide thin film: LiMnO, NaMnO or KMnO, depending on the used Support Salt during growth.





Figure 3.4: Samples before the plating process (Active Area: LIG only)

The Active Area is 0.5 cm^2 for all of them. Once the solution has been properly prepared, the cell for the deposition was prepared process as explained in Section 2.2.

The chosen deposition time (t_{DEP}) is 20 minutes, after which the cells have been disassembled and the LIG electrodes are left in a dryer for about 4 hours to allow the liquid of the solution to evaporate form it. At this point they are weighed to measure the change in mass before and after deposition. These results are reported in Table 3.2.

The applied current and the WE's potential for all of them have been recorded and plotted as a function of time:



Figure 3.5: Electroplating - Plots of the main quantities. (a) Current vs time; Potential vs time (b) Li_2SO_4 , (c) Na_2SO_4 , (d) K_2SO_4



 μSCs

Support Salt	Sample	Mass [mg] (before)	Mass [mg] (after)	Δm [mg]
Li ₂ SO ₄	1 2 3	$ \begin{vmatrix} 223.90 \pm 0.24 \\ 207.11 \pm 0.10 \\ 208.36 \pm 0.24 \end{vmatrix} $	$ \begin{array}{c} 229.23 \pm 0.25 \\ 211.42 \pm 0.14 \\ 211.00 \pm 0.07 \end{array} $	$ \begin{vmatrix} 5.331 \pm 0.503 \\ 4.309 \pm 0.240 \\ 2.634 \pm 0.305 \end{vmatrix} $
$\mathrm{Na}_2\mathrm{SO}_4$	1 2 3	$\begin{array}{c} 215.63 \pm 0.10 \\ 205.91 \pm 0.09 \\ 208.36 \pm 0.24 \end{array}$	$\begin{array}{c} 220.19 \pm 0.09 \\ 207.78 \pm 0.07 \\ 211.00 \pm 0.07 \end{array}$	$ \begin{array}{ } 4.558 \pm 0.137 \\ 1.876 \pm 0.114 \\ 2.634 \pm 0.305 \end{array} $
K_2SO_4	1 2 3	$\begin{vmatrix} 187.33 \pm 0.16 \\ 182.56 \pm 0.04 \\ 190.77 \pm 0.06 \end{vmatrix}$	$\begin{array}{c} 188.96 \pm 0.23 \\ 184.71 \pm 0.08 \\ 193.30 \pm 0.11 \end{array}$	$ \begin{vmatrix} 1.635 \pm 0.395 \\ 2.148 \pm 0.115 \\ 2.527 \pm 0.124 \end{vmatrix} $

Table 3.2: Manganese Oxide (support salt variation) - Amount of deposited material

From the data in Table 3.2 about the masses before and after the deposition process, it is possible to appreciate the very high accuracy of the balance used for this measurement.

The current applied to the cell toward the LIG interface of all the nine samples is reported in the plot of Fig.3.5(a). After the 30 seconds of the rest phase, during which the open circuit condition is imposed: I = 0, it is constant for 20 minutes at the value 0.5 mA, in order to have a current density of 1 mA cm⁻². The plots of Fig.3.5(b), 3.5(c) and 3.5(d) show the behaviour of the potential of the working electrode during the 20 minutes of the deposition. As explained in Section 2.2, it reaches a saturation after an initial increase for all the nine samples. Some noise can be present within these measurements visible above all in Fig.3.5(d) and it could be due to several reasons: mechanical instability of the cell during the process, contamination of the 3 M NaCl solution of the reference electrode, air bubbles in the Ag/AgCl glass tube, etc... In any case, a certain amount of Mn has been deposited on the LIG active area, regardless of the cleanliness of the recorded signal. In conclusion, with $J_{DEP} = 1 \text{ mA cm}^{-2}$ and $t_{DEP} = 20 \text{ min as experimental parameters}$, the mean values of the amount of deposited material, over the 3 samples, are reported in Table 3.3.

Support Salt	$\Delta \mathbf{m}_{mean}$ [mg]
$\rm Li_2SO_4$	4.139
Na_2SO_4	2.987
K_2SO_4	2.422

Table 3.3: Manganese Oxide, support salt variation - Mean value of the amount of deposited material and electroplating efficiency

Regarding the differences in the growth mode by varying the support salts, a

first consideration that can be done is about the amount of mass deposited on the LIG surface. Three samples for each case is obviously a small number to make a conclusion regarding a possible trend, but from these data:

- They are comparable for the three different support salts cases.
- The Δm decreases by increasing the ionic radius. This behaviour could be explained by considering the fact that the Li⁺, Na⁺ and K⁺ ions in the solutions acts as interstitial doping species between the growing manganese oxide layers, and so, during the same deposition time, a small number of layer can be deposited if the dopant ion is larger. Furthermore, the efficiencies of the dissociation reaction of the sulfates in water should be seen and maybe they could be different, probably resulting in a different deposition rate.



Figure 3.6: CV comparison between LIG blank and LIG after the electroplating

It is also important to make some consideration regarding the electroplating process:

- The amount of mass deposited on the LIG surface is very small. Other depositions have been performed on smaller LIG electrode with Active Area A = 0.5 cm x 0.5 cm instead of 1 cm x 0.5 cm the measured Δm was zero or negative. For this reason it is very important to measure very precisely the mass of the LIG electrode as explained in Section 2.2.
- It must be said that all the weightings might be affected by plating bath salts residuals due to an inefficient wash.



• It is very important for what concern the capacitive performances of the LIG electrode. Fig.3.6 shows a comparison between cyclic voltammetries CV for a LIG electrode before the electroplating process (blank sample), with an absolute capacitance $C_{blank} = 1.965$ mF, and after it, with $C_{Mn,dep} = 30.036$ mF: it is more than 1 order of magnitude higher. This means that the pseudocapacitive properties of the Transition Metal Oxides deposition have been properly activated. This can be also seen from the characterizations found in literature and reported in Fig.3.7 where the curves regarding LIG only are negligible with respect to the ones regarding LIG and manganese oxide, indicating that most of the capacitance comes from the pseudocapacitance of MnO₂. [18]



Figure 3.7: EC characterizations for electrodes with LIG only and MnO_2 electrodeposited at different deposition time. [18]

Calibration Plot. In this paragraph a calibration plot for the Manganese Oxide deposition was built in order to create a method to predict the amount of deposited mass as a function of the deposition time t_{DEP} . A quadratic mesh has been chosen for the t_{DEP} parameter: {4, 9, 16, 25, 36, 49, 64} min. For each of these point the Δm will be measured and a linear interpolation will be done to create an approximated trend.



Figure 3.8: Potential vs time for the calibration plot for the MnO deposition

Deposition Time (min)	Mass [mg] (before)	Mass [mg] (after)	$\Delta m [mg]$
4	172.27 ± 0.04	173.43 ± 0.26	1.159 ± 0.265
9	172.96 ± 0.06	175.02 ± 0.31	2.065 ± 0.314
16	170.19 ± 0.10	172.66 ± 0.05	2.464 ± 0.114
25	168.41 ± 0.08	169.83 ± 0.05	1.421 ± 0.093
36	165.68 ± 0.12	167.93 ± 0.09	2.25 ± 0.153
49	173.09 ± 0.02	175.74 ± 0.06	2.656 ± 0.068
64	165.42 ± 0.03	167.82 ± 0.25	2.406 ± 0.251

Table 3.4: MnO calibration plot measurements



Figure 3.9: Calibration plot for the MnO deposition

The plot of Fig.3.8 shows the measurement values of the potential evolution in time of the LIG electrode. It is possible to observe the usual initial increasing trend and the reaching of the plateau, apart for some noise. The calibration plot is reported in Fig.3.9. The amount of deposited mass increases with the increase of the deposition time t_{DEP} . This plot has been obtained with MATLAB. The interpolation line can be written as:

$$\Delta m_{MnO} = A_{MnO} \cdot t_{DEP} + B_{MnO} \tag{3.1}$$

where: $A_{MnO} = 15.63 \frac{\mu g}{min}$ is the deposition rate of this process and $B_{MnO} = 1.61 \mu g$ (parameters extrapolated from the experimental points).

Material Characterizations

FESEM. Electrodes synthesized with X-MnO thin film has been studied with Field Effect Scanning Electron Microscopy characterization, in order to observe its morphology at the micro and nanoscale. This analysis has been carried out after the electrochemical characterization, and so, some salt contamination or some filaments was observed due to the fact that fiberglass residue remained on the surface.

The FESEM analysis has been conducted with the following parameters:

- Electric Field: 10 kV
- Aperture: 30 $\mu {\rm m}$
- Working Distance WD: 2.5 mm
- Magnification: from 100 $\mu \mathrm{m}$ down to 200 nm
- Stage Temperature: 0°C

In Lens detector has been used and UHV has been created in the column to avoid contamination of the samples. All these information are written in the black raw below the images of the FESEM analysis.



Figure 3.10: FESEM. Na-MnO

From the pictures of Fig.3.10 it is possible to observe the high porosity level of the Manganese Oxide thin film's flower-like shape [18] morphology at the microscale and nanosheets at the nanoscale, and as a consequence, the high surface area of this material.



Figure 3.11: FESEM. Li-MnO

The images of the electrode with the Manganese Oxide layer deposited with K_2SO_4 , reported Fig.3.13, show some white features randomly scattered on the surface. From the picture of Fig.3.12, they could be attributed to salt residual due to an inefficient wash after being immersed in the aqueous Na_2SO_4 , 1 M electrolyte within the electrochemical cell.

The preparation of the samples for this observation was actually done by simply leaving the electrodes in a becher filled with deionized water for at least 30 minutes and so, by washing their surface. Probably, this treatment is not sufficient to remove all the residual traces of any material that could be present within the cell, and so some dynamical improvement of this simple method should be applied for future preparation before physical characterizations in order to avoid this situation and better observe the sample's surface and morphology, for example by producing some waves in the bath or by stirring it.



Figure 3.12: Electrodes immediately afterwards the EC characterization in Na_2SO_4 1 M electrolyte



Figure 3.13: FESEM. K-MnO
XPS. The excitation for the characterizations in this section was done through a X-ray source with Al K-alpha emission at 1486.6 eV.

A first Survey analysis, obtained through a wide energy scan, was done to identify qualitatively the elements that are prensent on the samples surface.



Figure 3.14: XPS. Survey spectrum for (a) Li-MnO, (b) Na-MnO, (c) K-MnO

The plots of Fig.3.14 show the Survey spectrum for the three samples synthesized by varying the support salt in the electroplating solution. In each of them it is possible to identify some peaks corresponding to the Manganese binding energy (Mn3s, Mn2p, Mn3p), different for each orbital, a peak corresponding to the Carbon (C1s) that is present due to the LIG substrate, a peak corresponding to the Oxygen (O1s) since the deposited material is a TMO and finally peaks due to the presence of the cations of the support salt: Li1s in Fig.3.14(a), Na1s in Fig.3.14(b), K2s and K2p in Fig.3.14(c). As explained before, the preparation to characterize these samples was not so good due to an inefficient washing and so, some traces of other elements are present, such as F1s and S2p.

A more quantitative analysis can be done through HR measurements (High Resolution) or starting from the Survey spectrum. Anyway, this second option is not so efficient in particular in case some peaks are overlapped, as for K2p e C1s in Fig.3.14(c).

HR analyses focus on individual element peaks, particularly the primary peaks of interest for a specific element. In situations where there might be potential overlap, like K2p and C1s, or Mn3p and L1s, efforts are made to acquire data from another region to help separate and distinguish the contributions of each element. The Oxygen detection was quite difficult due to the presence of too much contaminations as it can be observed in Fig.3.12, and so, this analysis is focused on the identification of the Manganese and its oxidation number. The known oxidation numbers for manganese are: $n_{OX} = \{+2, +3, +4, +6, +7\}$.



Figure 3.15: XPS. HR spectrum for Manganese (a) Mn3s, (b) Mn2p

	Peak (eV)	$\Delta E (eV)$
Mn 2p	642.13	11.68
Mn 3s	84.07	5.08

Table 3.5: XPS. Manganese Peaks

The main results of the plots of Fig.3.15, reported in Table 3.5, it is possible to compute the Average Oxidation State AOS [34] through the formula:

$$AOS = 8.95 - 1.13 \cdot \Delta 3s = 3.2 \tag{3.2}$$

So, the AOS is 3.2 that corresponds to Mn(III): the manganese stoichiometry is predominantly *Dimanganese Trioxide*, Mn_2O_3 . As it can be observed from Fig.3.16, it can be decomposed into Mn(III) and Mn(IV) contributions [42, 3]:

- ~ 70% Mn(III), which $2p_{\frac{3}{2}}$ peak is at 642 eV
- ~ 30% Mn(IV), which $2p_{\frac{3}{2}}$ peak is at 643.2 eV

In the decomposition of the HR peaks it is necessary to take into account:

- The curve shape in the analysis can be a mix of gaussian and lorentzian or exhibit asymmetry. The specific type and percentage of this mix depend on the element being analyzed and its relationship to other factors or elements in the data.
- Peak position: the position is recorded in a table but should always be referenced to a calibration peak. In our specific case, the calibration peak is the C-C peak of carbon at 284.8 eV.
- The relationship between peaks can vary, and certain peaks, like doublets or those associated with interconnected bonds, may have a fixed distance between them that must be maintained or respected.
- Peak area must align with stoichiometric ratios in examined compounds, consistent with the element's Relative Sensitivity Factor (RSF). This applies even when the same element appears in different compounds.



Figure 3.16: XPS. HR spectrum HR spectrum and deconvolution for Manganese (a) Mn3s, (b) Mn2p

The peaks of the III and IV components of the Manganese after their decomposition are reported in Table 3.6.

	Peak (eV)	$\Delta E (eV)$
Mn 2p (III)	642.01	11.68
Mn 3s (III)	83.99	5.3
Mn 2p (IV)	643.43	11.68
Mn 3s (IV)	84.5	4.5

Table 3.6: XPS. Manganese Peaks for Mn(III) and Mn(IV) contributions



EC Characterizations

The results from the electrochemical characterizations of the electrodes synthesized with manganese oxide electroplating onto LIG substrate will be discussed in this section.



Figure 3.17: OCV plots - Manganese Oxide electrode: (a) Li-MnO, (b) Na-MnO, (c) K-MnO

The result from the OCV measurements are the E_{OC} . Fig.3.17(a), 3.17(b) and 3.17(c) provides the behaviour of these quantities as a function of time, and their final values at the end of the technique's duration: 5 hours. It is the reference point for the following EIS and CV experiments. It typically depends on the system: the materials composing the electrodes and the electrolyte.





Figure 3.18: CV plots - Manganese Oxide electrode: (a) Li-MnO, (b) Na-MnO, (c) K-MnO

In Fig.3.18(a), 3.18(b) and 3.18(c) are reported the comparative results of CV measurements carried out at mVs⁻¹ up to 0.8 V as potential window.

The three curves, for each case of growth mode, are superimposable, so it can be said that the experiment is repeatable, with the experimental setup with the two electrodes compacted between two slides and held together by an elastic band.

The capacitance value, the coulombic and the energy efficiencies have been computed from these plots, and they have been reported in Table 3.7.

It is also important to observe the behaviour of these parameters as a function of the cycles. They are reported in Fig.3.19. These plots have been obtained through the MATLAB code in the Appendix 4.3 and for all of them it is possible to observe the same behaviour for all the three electrodes. In any case a saturation is reached after an initial stabilization behaviour during the first cycles. So, it could be useful to perform CV characterizations with more than 20 cycles, to obtain more stable quantities and so, more precise results.



Figure 3.19: CV Parameters as a function of cycle number - NaMnO electrode

The Spectroscopy characterization was performed on the cell before (Fig.3.20(a)) and after (Fig.3.20(b)) the CV, in order to observe the effect of several voltammetry cycles on the impedance of the electrode. It was carried out in the frequency range [10 mHz, 1 MHz], with 10 points per decade.

As in the previous case, these results are very similar for the three electrodes, confirming that the experiment is repeatable with the used equipment.



Figure 3.20: Nyquist plots - NaMnO electrode. (a) Before CV, (b) After CV

Sample	Capacitance			ESR (Ω)		$ $ η_C	$ \tau$
Sampie	mF	${\rm mFcm^{-2}}$	Fg^{-1}	Before	After	%	ms
				CV	CV		
		S	upport Sa	alt: Li_2SC) ₄		
$\mathrm{S}_{1,Li}$	131.371	262.742	24.643	5.318	5.463	91.277	698.63
$\mathrm{S}_{2,Li}$	148.607	297.215	34.488	5.608	5.477	90.713	833.39
$\mathrm{S}_{3,Li}$	94.396	188.792	32.118	8.204	8.138	92.293	774.42
		Sı	upport Sa	$t: Na_2SC$	D_4		
$S_{1,Na}$	140.249	280.497	30.770	1.150	0.367	89.811	161.28
$S_{2,Na}$	158.009	316.017	84.226	5.854	5.506	90.283	924.98
$\mathbf{S}_{3,Na}$	133.466	266.932	52.816	7.389	7.603	89.932	986.18
${\bf Support \ Salt: \ K_2SO_4}$							
$S_{1,K}$	140.734	281.467	86.076	5.293	5.072	90.307	744.91
$\mathbf{S}_{2,K}$	176.184	356.460	82.022	6.423	6.297	89.435	1131.62
$\mathbf{S}_{3,K}$	178.230	266.932	51.157	6.289	5.363	91.711	1120.89

From these Nyquist plots it is possible to extract the ESR parameter, by computing the horizontal intercept of the semicircle before the vertical line.

Table 3.7: Electrode Parameters - X-MnO

In order to make a comparison between the parameters evaluated for the three support salts, the mean value was computed between the three samples.

From Table 3.8 it is possible to observe a trend of the capacitance with respect to the Ionic Radius of the support salt. In particular, the capacitance increases while increasing the ionic radius. This effect could be attributed to the fact that the spacing between Manganese Oxide layer increases for larger interstitial dopant species, and so, the capacitance increases.

ТМО	Capacitance		ESR	η_C	
1010	$mFcm^{-2}$	Fg^{-1}	Before CV	After CV	%
Li-MnO	249.583	30.416	6.377	6.359	91.428
Na-MnO	287.815	55.937	4.798	4.492	90.009
K-MnO	330.098	73.084	6.002	5.577	90.484

 Table 3.8:
 Electrode Parameters - support salt comparison







Figure 3.21: CV plot for each support salt (last cycle)



Figure 3.22: EIS plot for each support salt (after CV)

In Fig.3.22, a colour map has been done for the Spectroscopy, in order to show the variability range of the real part of the impedance: in all the three cases they are comparable and the fluctuations in the real part at low frequencies consistently fall within a similar range. Hence, it's not feasible to attribute different currents to the various samples, as their impedance values are significantly different.

From Fig.3.21 it is possible to observe how by increasing the ionic radius, the peak at the end of the charge phase became more evident. It means that a different behaviour at the interface between the Active Area and the electrolyte, regarding the oxidation reactions, is present.



Figure 3.23: Specific Capacitance vs. Ionic Radius

Finally, the plot of Fig.3.23 shows the increase of the capacitance per unit mass with respect to the Ionic Radius of the ion of the support salt of the deposition solution. This behavior could confirm the hypothesis made at the beginning of the chapter. In fact, the fact that the capacity increases as the ion radius increases could be due to the different distance between the manganese oxide layers.

A similar approach with results and characterizations that can confirm the goodness of this synthesis technique based on the addition of support salts in the solution have been exploited for the manufacture of the so called Zn/NMO batteries. Zinc-based batteries (ZIBs), are promising alternatives to LIBs that have dominated the electrochemical energy storage market due to their high energy density but should be replaced due to the global lithium shortage and safety issues. Anyway ZIBs face challenges like limited host materials and zinc dendrite issues. In a wide range of



excellent materials for use as a cathode, manganese oxide is an excellent candidate thanks to its high theoretical capacity (308 mAh g⁻¹) and high output voltage (up to 1.5 V). Between the various manganese oxide's crystallographic polymorphs, layered δ -MnO₂ with a large interlayer spacing d = \sim 7 Å can provide fast Zn²⁺ ions migration migration pathway and meanwhile avoid phase transformation. The electrochemical performance of these electrodes was improved by inserting Na⁺ ions and water crystals between the manganese oxide layers. [43]

 $Na_{0.55}Mn_2O_4 \cdot 1.5H_2O$ were synthesized by a facile molten salt reaction process and compared with $Na_{0.55}Mn_2O_4$ and $Mn_2O_4 \cdot nH_2O$ to observe the results difference by varying the interlayer spacing. TEM and HRTEM analysis indicate a uniform laminar structure for this sample, with a lattice fringe measuring 0.25 nm, corresponding to the (200) plane of octahedral MnO_6 . In contrast, $Na_{0.55}Mn_2O_4$ and $Mn_2O_4 \cdot nH_2O$ exhibit smaller interplanar spacings (0.54 nm for the (001) plane), which is attributed to the removal of water molecules or sodium from the interlayer of manganese oxides as shown in Fig.3.24.



Figure 3.24: $Na_{0.55}Mn_2O_4 \cdot 1.5H_2O$ schematic illustration and structural analysis of the nanosheet and its counterpart [43]

Electrochemical characterizations were done on these structures to study their capacitive performances based on the Zn^{2+} (de)intercalation. These measurements were carried out in hybrid aqueous electrolyte (2M ZnSO₄ and 0.1M MnSO₄ with 0.5M Na₂SO₄ additive) at 0.1 mV s⁻¹. The results are reported in Table 3.9.

Structure	$\begin{tabular}{lllllllllllllllllllllllllllllllllll$
$Na_{0.55}Mn_2O_4 \cdot 1.5H_2O$	309.2
$Na_{0.55}Mn_2O_4$	170.2
$Mn_2O_4 \cdot nH_2O$	180.1

Table 3.9: ZIB cathode - Capacity. [43]

All three samples exhibit excellent capacity retention after 300 cycles, demonstrating good reversibility and structural stability in the hybrid aqueous electrolyte.



Calcination Process

The effect of temperature on the grown TMOs layer onto the LIG substrate will be discussed in this section. To this aim, the prepared electrodes was placed within an oven called BUCHI, for a given time t_{calc} .

The goal of this experiment is to see if, by applying this thermal treatment some difference induced in the stoichiometry and morphology of the metal oxide will produce different effect in the electrochemical performances of the electrode.



Figure 3.25: LIG rectangular features. Active Area = 0.25 cm^2

Electrodes Preparation. Smaller LIG substrates have been used for this experiment with respect to the ones described before. Their Active Area is now 0.25 cm^2 and they are shown in Fig.3.25. The laser parameters to obtain such geometries are the same described before.

The usual experimental setup depicted in Fig.2.3 and the same solution were used but now, the MnO layers have been synthesized by applying a negative and a positive current density of 1 mA cm² as absolute value, in order to observe the differences, in terms of EC performances, of this parameter within the deposition process.

Anyway, it is important to say that this electrodes geometry makes it much more difficult to measure the quantity of material deposited because it is much lower than in the cases: Active Area = 0.5 cm^2 .

Thermal Process. After the electroplating, the electrodes are inserted into the BUCHI and to be heat treated.



Figure 3.26: Thermal Process during time

They were subjected to the program described in Fig.3.26: (a) 1 hour at 60°C; (b) $T = 300^{\circ}C$ for a variable time t_{calc} ; (c) again 1 hour at 60°C to cool the sample before returning it to room temperature. Cooldowns are not fast, so the 60°C ramps are for hill control only.

Three values have been chosen for the parameter $t_{calc} = \{0, 2, 4\}$ h, in order to observe the differences regarding the EC performances by varying it.

EC Characterizations. All the measurements were carried out by using the same technique's parameters and sampling, and so, for each case, the represented CV plot is a mean value over the three samples curves.

The results coming from the deposition done with negative currents were not so good: for all the studied samples the behaviour is much more resistive with respect to the positive current case. In general the synthesis method with applied negative current density for Manganese Oxide deposition was abandoned.



Figure 3.27: Electrodes synthesized with: Electroplating at 1 mA cm⁻² and Calcination at several t_{calc} . (a) CV (b) EIS (after CV)

A more capacitive behaviour is instead observed for the electrodes fabricated with positive current density with respect to the negative current density case, for each applied t_{calc} . In conclusion, it is possible to say that calcination has no effect especially by considering that the specific current, depicted in Fig.3.27(a), is similar to the one corresponding to the CV of the electrode characterized without this thermal treatment.

The performances of these electrodes were also evaluated by performing self discharges, discussed in the next section.



Self Discharge

Definition. Self discharge refers to the voltage drop that occurs in the SCs electrochemical cell while it is stored in a charged state. This phenomenon is often related to the chemical faradaic reactions taking place on the surface, rather than being influenced by any physical processes that could lead to the voltage drop, such as charge redistribution. Anyway, often in literature the term "Self Discharge" refers to both the physical and chemical processes since sometimes these mechanisms are unknown and difficult to distinguish and separate.

Supercapacitors have faster self-discharge compared to batteries, impacting their energy and power availability. To mitigate this, regular recharging or a constant float current is required to keep them fully charged. SCs face commercial limitations in various sectors due to self-discharge issues, necessitating recharging systems. While self-discharge rates are widely studied, the underlying mechanisms are often overlooked. To combat self-discharge, intelligent material modifications are crucial for enhancing performance and reducing self-discharge rates. [2]

Theoretical Mechanisms. By taking the OCP as reference, a high potential between two electrodes of the SC is held during the charged state. This high-energy state will naturally undergo relaxation through any available means, seeking to return to its low-energy, uncharged state. Some mechanism [2] have been identified:

- Ohmic Leakage. It is the least commonly discussed mechanism since it is the most straightforward one. It simply arises from a flaw in the SC cell construction, where a resistive pathway forms and connects the positive and negative electrodes. This direct connection facilitates the discharge of the electrochemical cell, leading to self-discharge.
- *Parasitic Faradiac Reactions*. They refer to an oxidation or reduction reaction that takes place on the electrode surface, resulting in the discharge of the electrode. The positive electrode in a supercapacitor balances positive charge via electrolyte anions in the double-layer. However, the high positive potential on the electrode can surpass the oxidation potential of certain species, causing them to undergo oxidation. This oxidation process transfers electrons into the electrode surface, reducing the positive charge on the surface.

In systems with carbon electrode, aqueous electrolyte, SCs can undergo self discharge due to the following reactions: water electrolysis and oxygen reduction. [27]

– A typical faradiac O_2 reduction can be described by the following reaction: [2]

$$4M^{-}(surf)H^{+}(ads) + O_{2}(aq) \to 2H_{2}O(l) + 4M(surf)$$
(3.3)



where M is the metal on the electrode surface that loses charges due to the oxidation of the aqueous O_2 in solution and consequent production of H_2O .

- Pillay and Newman proposed that water decomposition can act as a side reaction leading to self discharge in Electrical Double Layer capacitors. This occurs when the necessary thermodynamically stable potentials for water electrolysis, 0.00-1.23 V based on standard conditions at 298 K, are reached during the SC charging, causing the electrodes to spontaneously discharge due to the water's decomposition and the evolution of oxygen and hydrogen on the positive and negative electrodes, respectively, and as a consequence, a loss in the electrode's charge will occur. [27]

$$2H_2O \to O_2 + 4H^+ + 4e^-$$
 (3.4)

$$2H^+ + 2e^- \to H_2 \tag{3.5}$$

This suggests that water electrolysis could be a cause of self-discharge in aqueous Supercapacitors.

• Charge Redistribution. In porous electrodes and many pseudocapacitive materials, the outer section of the electrode charges faster than the bulk material. This means that the outer part reaches the desired charge level before the bulk does. When charging stops, charges then move through the material to balance the potential difference, a process referred to as charge redistribution.

During charge redistribution, as charges travel deeper into the material, the voltage measured at the outer surface of the electrode decreases. This voltage drop occurs because the potentials within the material are equalizing, leading to the gradual release of stored energy and the self-discharge of the electrode. In many cases, the presence of numerous resistive components, such as solution resistance in pores or electronic/ionic resistance in pseudocapacitive films, makes charge redistribution a significant contributor to overall self-discharge. Consequently, the shape of the self-discharge profile is primarily determined by this mechanism.

The separation of such contributions could be important to better design the measurement cell and limit the self discharge, but at the same time it is a very challenging study.

There are many well studied cases reported in literature [2] in which the measured self discharge has the same profile for different material, even if the dominant mechanisms are different. The plots in Fig.3.28 shows the behaviour of the Cell Potential, measured with respect to a Reference Electrode, for three different electrode materials: Carbon, Ruthenium Oxide RuO_2 and Manganese Oxide MnO in aqueous electrolytes with a given concentration.



Figure 3.28: Self-discharge profiles of Positive (Solid Lines) and Negative (Dashed Lines) charged electrodes of (a) *Carbon* in 1 M aq. H_2SO_4 , (b) RuO_2 in 0.5 M aq. H_2SO_4 and (c) MnO in 0.5 M aq. Na_2SO_4 . [2]

It is known from literature that when these materials are used as positive electrodes, they exhibit specific charge redistribution and self-discharge mechanisms. However, as negative electrodes, carbon undergoes a faradaic reaction, RuO_2 experiences charge redistribution, and MnO's self discharge mechanism is not yet fully understood.

In conclusion, it's worth noting that self-discharge increases with higher temperatures. [2] This effect has been experimentally observed and is expected due to the temperature's influence on reaction rates and transport mechanisms.

Measurement Methods. Self-discharge assessment can occur in either *Full Cell* or *Half Cell*. Examining full cell self discharge is valuable for simulating commercial devices. However, understanding full cell results mechanistically is complex because independently analyzing self discharge kinetics for both electrodes isn't feasible. The recorded voltage is the difference between positive and negative electrodes, making attributing voltage drop to a single electrode impractical.

Self discharge is assessed using *Open-Circuit Potential* or *Float Current* measurements. In both cases, the system is charged to the desired potential or voltage, and self discharge is monitored over hours. Open-circuit measurements record potential changes, while float current measurements apply a minor current to maintain voltage. Float current is continuously tracked. [2]

Models and Equations. Several mathematical models [2] studied and provided the Conway group can be used in order to identify the self discharge rate limitation mechanism.

• When the full cell configuration is used within the measurement apparatus, some short circuit paths could be present between the two electrodes. In this case, *ohmic leakage* phenomenon will occur, and a charge moving through this path could generate self discharge which rate can be described as:

$$\ln\left(\frac{V}{V_i}\right) = \frac{-t}{RC} \tag{3.6}$$

 μSCs

where V is the recorded voltage, V_i is the voltage at the beginning of evaluated period, t is the time and the RC group is composed by the resistance of the Ohmic Leakage and the capacitance of the cell. Eq.3.6 describes a decreasing exponential profile of the recorded voltage as a function of time.

- In case of self discharge due to *Parasitic Faradaic Reactions*, the profile of the measured voltage can be different if the phenomenon is Activation-controlled or Diffusion-controlled.
 - The faradaic self discharge is *activation-controlled* if there is a high concentration of the reacting species or if they are attached (or close) to the electrode active material. In this case, the measured potential can be expressed through the following equation:

$$V = -\frac{RT}{\alpha F} \ln\left(\frac{\alpha F i_0}{RTC}\right) - \frac{RT}{\alpha F} \ln\left(t + \frac{C\tau}{i_0}\right) \qquad \tau \equiv \left(\frac{RT}{\alpha F}\right) \frac{i_0}{i_i} \qquad (3.7)$$

where T is the temperature, R and F are the the gas and the Faraday's constants respectively, i_0 is a parameter called exchange current density, C is the capacitance at the active material-electrolyte interface and τ is the integration constant, where i_i is the polarization (initial) current in this definition.

Self discharge profiles are often presented as potential (V) plotted against the logarithm of time. These plots typically exhibit a linear voltage decrease after an initial plateau, and they provide essential information, such as interfacial capacitance or exchange current density. Importantly, this self-discharge behavior is independent of the initial potential.

- The faradaic self discharge can be *diffusion-controlled*. Conway shows that within these kind of phenomenon the potential is characterized by a linear profile if plotted with respect to the square root of the time t:

$$V = V_i - \frac{2zFAD^{\frac{1}{2}}\pi^{-\frac{1}{2}}c_0}{C}\sqrt{t}$$
(3.8)

In these equation, D is the diffusion coefficient, z is the charge, c_0 initial concentration of the reacting species and A is the Active Area. The other paarmeters are the same of the previous formula. Conway's model is derived from Fick's Law and applies to highly porous electrodes with depleted reactants. Self discharge in such electrodes is primarily driven by external surface diffusion, similar to flat surfaces.

- self discharge can be also due to *Charge Redistribution*. Also in this case the shape of the measured potential with respect to the time can be different if the rate limited process is resistance-limited or diffusion-limited.
 - Self discharge in materials like ruthenium oxide and cobalt oxide films is diffusion-controlled. Charge redistribution occurs due to quicker changes



in oxidation state on the film's surface during charging compared to the bulk. Upon open-circuit, oxidation states even out through the film's thickness, neutralizing charge with protons. Proton diffusion becomes the limiting step in these materials, leading to the unique square root of time profile seen in self-discharge behavior. This highlights the pivotal role of diffusion kinetics in governing self discharge dynamics in these materials.

- Charge redistribution can be slowed by *incremental Resistance* elements like solution resistance in pores or electronic/ionic resistance in pseudocapacitive films. De Levie's 1963 work introduced a transmission line circuit concept for analyzing resistance systems. Later models incorporated nested transmission lines to explain charge redistribution in complex electrochemical systems, especially in porous electrodes and pseudocapacitive films. These models often reveal an exponential relationship between self-discharge voltage and time, enhancing our understanding of charge redistribution mechanisms.
- Finally, in many complex and more realistic system, self discharge could be due to *mixed Faradaic reaction and charge redistribution mechanisms*. In combined systems, predictions consider activation-controlled faradaic self-discharge and charge redistribution self-discharge. The profile shape depends on their relative rates. When activation-controlled self-discharge is slower than redistribution, a steep slope occurs. As redistribution slows due to potential equalization, the slope flattens.

Results. Self discharge has been studied, for Manganese Oxide electrodes, on both the two analyzed geometries:

- On the samples prepared with the calcination process discussed in Section 3.1.1: Active Area A = 0.25 cm², titanium grid as current collector, for blank electrodes and for samples characterized by MnO deposition onto LIG with calcination time $t_{calc} = \{0, 2\}$ h.
- On the samples fabricated without calcination in Section 3.1.1: Active Area A $= 0.5 \text{ cm}^2$, titanium grid as current collector, MnO electroplating and drying in a dryer at room temperature for at least 4 hours.

The experimental setup used to perform these analysis is *half cell* as explained in the *Measurement Methods* paragraph. Active Carbon was used for the counter electrode and Ag/AgCl as reference electrode. For the experiments performed on the electrode with Active Area $A = 0.25 \text{ cm}^2$ and fabricated with the calcination process, the charging mechanism and the self discharge evaluation consist in the following steps:



Figure 3.29: Temporal evolution of the self discharge measurement method by varying t_f

- An initial 5 minutes OCV, in order to evaluate the E_{OC} as the reference point to start the charging process.
- A linear increase of the voltage, $\nu = 1 \text{ mV/s}$ called *PotentioDynamic* or *Linear Swipe Voltage (LSV)* to reach the charged state. This process starts from E_{OC} and finishes when the potential reaches 0.8 V with respect to E_{OC} .
- A *PotentioStatic* step, during which the potential of the electrode has been kept constant to the value reached in the previus step. The duration of this procedure is called floating time t_f , and it will be modified during these expreiment in order to observe the variation of the self discharge as a function of this parameter.
- Another OCV of t = 1 hour to evaluate the self discharge.
- Finally, there are other steps in order to start again the entire charging and measurement process with a different t_f parameter, carrying the potential close to the E_{OC} value.

All the steps described before are represented in Fig.3.29 with their parameters. Five floating times have been selected to study the self discharge: $t_f = \{0, 30, 60, 600, 3600\}$ s.





Figure 3.30: Self discharge - Potential vs time, measured for blank electrode in different atmospheres: (a) Air, (b) N_2

The plot of Fig.3.30(a) shows the behaviour of the measured potential with respect to the Log of the self discharge time t_{SD} , that is the duration of the second OCV procedure for the blank electrode, for each t_f .

It is possible to recognize a linear drop after a plateau, that is the profile describing a *activation-controlled Faradaic reaction* as rate limitation mechanism for the self discharge. So, in principle, these curves could be described through Eq.3.7 and the unknown parameters could be extracted from them.



Figure 3.31: Self discharge: Potential Energy Loss during the SD time vs \mathbf{t}_f for blank electrode





Figure 3.32: Measurement cell with N_2 flux

The plot of Fig.3.31 shows the behaviour of the *Potential Energy Loss*. It was computed as $\Delta V_{loss} = V_f - V_i$, where $V_{i/f}$ are the potentials measured at the beginning and ate the end of the second OCV procedure and the initial. It decreases while increasing the t_f parameter.

In order to verify if Faradaic Reactions are really present at the interface between the Active Area and the electrolyte, the same experiment was done by fluxing N_2 within the measurement cell, as shown in Fig.3.32, and so, performing the characterization in a different atmosphere, poor of oxygen molecules O_2 .

The results of the measurements conducted in N₂ atmosphere have been reported in Fig.3.30(b) and in Fig.3.33 it is possible to appreciate how much, by considering the same $t_f = 3600$ s, the self discharge

decreases in N_2 atmosphere rather than in Air. Also in this case, the self discharge time has been reported in Log scale.



Figure 3.33: Self discharge - Potential vs time, measured for blank electrode in different atmospheres

The trend of the Potential Energy Loss with respect to t_f has been reported in Fig.3.34 (red data). It has the same profile of the one in O₂ atmosphere, but it is lower, showing that the faradaic oxidation reactions were reduced, and the self discharge was limited.



Figure 3.34: Self discharge: Potential Energy Loss during the SD time vs t_f for blank electrode in different atmospheres

The data studied up to now are related to the self discharge analysis for a blank electrode. In the following, we will see what happen if a deposition of MnO thin film has been done on the top of the LIG surface.

According to the experimental results from literature, discussed in the *Models* and Equation paragraph, the presence of a Metal Oxide, and as a consequence, of a pseudocapacitance, should be the cause of self discharge due charge redistribution. Anyway, we are studying a more complex system with both the mechanisms. As a consequence, we will expect a difference in the slope of the potential profile during the second OCV step.

The technique to charge and measure the potential is the same of the blank case and the also the considered t_f are the same.

The plot of Fig.3.35 shows the self discharge measurement for an electrode characterized by a MnO thin film onto the LIG surface, through electroplating carried on with $J_{DEP} = 1 \text{ mA cm}^{-2}$ Deposition Current Density for $t_{DEP} = 20$ min, followed by a calcination process carried on at 300°C for 2 hours. It can be observed that the presence of the Manganese Oxide slightly decreases the slope of the linear drop after the initial plateau with respect to the blank case and so, it can be said that the charge redistribution is present but its rate is lower than the Faradaic reaction one.



Figure 3.35: Self discharge - Potential vs time, measured for MnO electrodes. Electroplating: positive current, calcination: 2h, 300°C

Finally, the plot of Fig.3.36 shows the variation of the Potential Energy Loss (as a function of the t_f parameter), by adding the MnO thin layer on top of LIG and by increasing the calcination time t_{calc} . From the curves of this plot it is possible to observe that the trend is the same of the blank case and that the effect of the calcination process is to decrease the self discharge phenomenon. So, probably, the different MnO form obtained through this thermal treatment with those parameters $(t_{calc} = 2 h \text{ and } T = 300^\circ)$ is better to limit the self discharge and it could be taken into account into the design of the fabrication of the electrode for these devices.



Figure 3.36: Self discharge: Potential Energy Loss during the SD time vs \mathbf{t}_f for blank and MnO electrodes in air



Regarding the analysis on the electrode with Active Area $A = 0.5 \text{ cm}^2$, fabricated without the calcination process, the charging and measurement methods have been done in parallel on two electrodes shyntesized with MnO plating with Li₂SO₄ as support salt within different atmospheric conditions. The procedure is the same described before:

- An initial CV and EIS to characterize the two electrodes.
- OCV: 1 hour.
- *PotentioDynamic*: 1 mV s^{-1} , to 1.05 V vs Ref. This potential has been chosen since it is the point at which the oxidation peak appears.
- PotentioStatic: 1 hour.
- OCV: 48 hours to evaluate the self discharge.



Figure 3.37: CV measurement for different atmospheric condition



Figure 3.38: Self discharge measurements

Fig.3.37 shows the initial characterization for the two electrodes and with their specific capacitance. It was done in order to see if the capacitance were comparable and so, to perform the self discharge characterization in parallel.

Now, the quantity that has been measured to evaluate the self discharge is the current. During the LSV procedure, the linear increase of the voltage produce an increase of the current that can be seen in Fig.3.38(a). As expected, the oxidation peak is present only in the case of Air atmosphere, rich of O_2 . During the successive Potentiostatic step, the potential was kept constant and the current decreases, resulting in a leakage. It has been reported in Fig.3.38(b). The vertical axis is in log scale now and it can be observed that the measured leakage is higher in the air case. So, also in this case, the effect of the atmosphere influences the self discharge phenomenon.

In conclusion, the analysis carried out in different atmospheric conditions demonstrate that self discharge in aqueous electrolyte systems [1] is caused by the presence of oxygen molecules O_2 within the cell or trapped in the electrodes pores and the atmosphere is an important parameter during the design phase of the desired device in order to limit the unwanted self discharge.



3.1.2 FeO Electrode - Cathode

The synthesis and the characterizations for the negative electrode with Iron Oxide were performed in the same way of the Manganese Oxide one.

Electroplating

The schematic of the process we want to do in order to obtain an Iron Oxide thin film is reported in Fig.3.39. Also in this case, titanium grid has been contacted to the LIG substrate to connect the electrode to the power supply.



Figure 3.39: Cross Section of the Electrode after the FeO Deposition

These deposition technique were not so tested and so, several tests have been carried out by modifying some process parameter in order to understand the best ones.

Solution Preparation. As in the positive electrode electroplating, also in this case a solution containing the atoms we want to deposit has been prepared.

- 80% Iron Nitrite: $Fe(NO_3)_3$, $MW = 241.86 \text{ g mol}^{-1}$
- 20% Iron Chloride: FeCl₃, MW = 162.2 g mol⁻¹

Their total concentration was 0.1 M in deionized water.



Figure 3.40: Iron Oxide Electroplating Solution: (a) Iron Nitrate, (b) Iron Chloride. (c) Solution

The reagents are reported in Fig.3.40 and the obtained solution is reported in Fig.3.40(c). It is important to do some considerations regarding this solution, with respect to the Manganese Oxide one:

- It is more stable: it doesn't precipitate after a few hours as the MnO solution. It lasts longer and does not need to be re-mixed or re-prepared if it is not used all over the course of a day.
- Its pH has been measured and it is quite acid (pH = 1.45).

The Active Area for all the following described processes is 0.5 cm^2 .

Test 1. A preliminary test revealed the fact that, using the same setup and applying the same deposition current in absolute value, a deposited mass is detectable only in cathodic ($J_{DEP} < 0$).

As for the MnO deposition, electroplating has been performed onto three samples by keeping the deposition time t_{DEP} constant at 20 minutes and by applying a current density: $J_{DEP} = -1 \text{ mA cm}^{-2}$.

Sample	Mass [mg] (before)	Mass [mg] (after)	$\Delta m [mg]$
$S_{1,FeO}$	173.33 ± 0.15	175.03 ± 0.11	1.701 ± 0.19
$S_{2,FeO}$	175.84 ± 0.11	176.35 ± 0.03	0.508 ± 0.12
$S_{3,FeO}$	204.10 ± 0.03	205.40 ± 0.03	1.304 ± 0.05

Table 3.10: Iron Oxide - TEST 1. Amount of deposited material



Figure 3.41: Iron Oxide Electroplating. TEST 1

The results of this plating have been reported in Table 3.10. A first consideration that can be made is that, compared to the deposition of MnO, in this case the deposited mass is much lower.

It is also important to observe the fact that, in all the three cases, the Δm is very small and so, this process, with these parameters, is characterized by a low deposition rate. The mean Δm computed over the 3 samples fabricated with negative current is $\Delta m_{mean} = 1.171$ mg.

Test 2. The idea for the second Test on FeO electroplating is to modify the deposition current and time in order to keep constant the amount of charge provided to the electrode.

In particular, the current has been decreased to 0.5 and 0.1 mA cm⁻² and the time has been increased to 40 and 200 minutes, respectively.

Deposition Parameters $[mAcm^{-2}, min]$	Mass [mg] (before)	Mass [mg] (after)	$\Delta m [mg]$
$0.1, 200 \\ 0.5, 40$	$\begin{array}{c} 159.07 \ \pm 0.06 \\ 165.50 \ \pm 0.22 \end{array}$	$\begin{array}{c c} 159.13 \pm 0.02 \\ 166.64 \pm 0.04 \end{array}$	$\begin{array}{c c} 0.052 \pm 0.068 \\ 0.132 \pm 0.220 \end{array}$

Table 3.11: Iron Oxide - TEST 2. Amount of deposited material





Figure 3.42: Iron Oxide Electroplating. TEST 2

From the results in Table 3.11 it seem to observe that by decreasing the deposition current also the Δm decreases, it doesn't matter how long the process takes.

Calibration Plot. As for the MnO deposition, also in this case a calibration plot has been created. The time mesh is the same: $t_{DEP} = \{4, 9, 16, 25, 36, 49, 64\}$ min.



Figure 3.43: Potential vs time for the calibration plot for the FeO deposition

Politecnico di Torino	CHAPTER 3	μSCs	
Deposition Time [min]	Mass [mg] (before)	Mass [mg] (after)	Δm [mg]
4	197.72 ± 0.06	198.73 ± 0.07	1.005 ± 0.093
9	170.72 ± 0.03	171.52 ± 0.04	0.796 ± 0.045
16	179.34 ± 0.06	180.22 ± 0.04	0.878 ± 0.070
25	168.83 ± 0.06	169.80 ± 0.06	0.971 ± 0.091
36	180.71 ± 0.02	181.57 ± 0.06	0.865 ± 0.061
49	187.24 ± 0.03	188.29 ± 0.02	1.059 ± 0.034
64	201.31 ± 0.02	202.65 ± 0.02	1.342 ± 0.035

Table 3.12: FeO Calibration Plot measurements

Also in this case, apart for some point in the plot, an increasing trend can be observed by increasing the deposition time.



Figure 3.44: Calibration plot for the FeO deposition

The interpolation line can be written as:

$$\Delta m_{FeO} = A_{FeO} \cdot t_{DEP} + B_{FeO} \tag{3.9}$$

where: $A_{FeO} = 6.193 \ \mu g \ min^{-1}$, and $B_{FeO} = 0.808 \ \mu g$ were extrapolated from the experimental points. The A_{FeO} is one order of magnitude lower than the A_{MnO} parameter: 15.63 $\mu g \ min^{-1}$ from Eq.3.1. This evidence confirms the lower deposition rate of this process with respect to the Manganese Oxide plating.



Material Characterizations

FESEM. Also in this case, the FESEM analysis has been conducted using the same parameters. The samples has been observed after the CV analysis and their surface has been washed by keeping them into a deionized water bath for at least 30 minutes.



Figure 3.45: FESEM - FeO

The images of Fig.3.45 shows the morphology of the FeO surface at different magnifications. It is similar to the one of LIG alone [32] and this observation confirms the fact that through the plating process with the previously described parameters a very small amount of material is deposited with respect to the MnO case.

EC Characterizations

The results from the electrochemical characterization of all the synthesized electrode will be discussed in this section.

Test 1. The samples fabricated within Test 1 have been characterized. Fig.3.46 shows the CV plots for all of them.

All of these measurements have been done with the same parameters:

- Scan Rate: 10 mV s⁻¹
- Cycles: 110
- Potential Window:
 - S_{1,FeO}: from 0.3 V (vs Ref) to -1.1 V (vs Ref)
 - S_{2,FeO}, S_{3,FeO}: from E_{OC} to -1.1 V (vs E_{OC})



Figure 3.46: CV Characterization - FeO (TEST 1). (a) $S_{1,FeO}$: $\Delta m = 1.701$ mg; (b) $S_{2,FeO}$, $S_{3,FeO}$: $\Delta m = 0.508$ mg, 1.304 mg

Apart for the differences in the applied potential window, the currents recorded for $S_{1,FeO}$ and $S_{3,FeO}$ with a similar FeO deposited mass (Table 3.10), are comparable, while sample $S_{2,FeO}$, with a lower FeO amount of deposited material, reaches higher currents.

The results from the Impedance Spectroscopy are very different with respect to the ones of MnO electrode. This is due to the fact that FeO is much more resistive. A higher Z' is in fact reached in all the cases. It is important to remember that the imaginary part is roughly inversely proportional to the capacitance: from Eq.2.13 we have - Z'' $\propto \frac{1}{C_{eq}}$. It means that such behaviour describes a less capacitive structure.

Fig.3.47(a) shows the Nyquist Plot for the EIS characterization for Sample $S_{3,FeO}$, before and after the CV, while the results regarding samples $S_{1,FeO}$ and $S_{2,FeO}$ are reported in Fig.3.47(b), only after CV.







Figure 3.47: EIS Characterization - FeO (TEST 1). (a) $S_{3,FeO}$: $\Delta m = 1.304$ mg, before and after CV; (b) $S_{1,FeO}$, $S_{2,FeO}$: $\Delta m = 1.701$ mg, 0.508 mg, after CV

Also in this case, by observing the results after CV, the curves of $S_{1,FeO}$ and $S_{3,FeO}$ are similar due to their comparable mass loading, while for $S_{2,FeO}$ both the real and imaginary parts of the impedance are higher, probably due to the very low deposited material.

Zooms have been performed on the semicircle region in order to observe it better and to estimate the ESR. Also here, it is possible to notice similarities just between $S_{1,FeO}$ and $S_{3,FeO}$, while the semicircle is larger for $S_{2,FeO}$.

Sample	Capacitance			ESR (Ω)		$\mid \eta_{C/E}$	$ \tau$
Sample	mF	${ m mFcm^{-2}}$	Fg^{-1}	Before CV	After CV	%	ms
S _{1,FeO}	91.06	182.12	53.53	7.455	5.984	98.193	544.90
$\mathbf{S}_{2,FeO}$ $\mathbf{S}_{3,FeO}$	$32.48 \\ 55.28$	$64.96 \\ 110.56$	$63.94 \\ 42.39$	$7.232 \\ 8.078$	$6.616 \\ 7.074$	96.979 94.869	214.89 391.05

Table 3.13: Electrode Parameters - FeO (TEST 1)

All the parameters extracted from these characterizations for the 3 studied electrodes have been stored in Table 3.13.

Test 2. A first important observation from the plating's results of this test is that the amount of deposited material decreases by decreasing the deposition current (from Table 3.11).



Figure 3.48: EC Characterizations - FeO (TEST 1 & 2). (a) CV plots; (b) Nyquist plots

In order to observe the differences, in terms of capacitive performances, of such synthesized samples, the specific current has been reported in Fig.3.49 to study the measurements of the CV. As for the plots in Fig.3.46, a higher current is measured for the samples with lower deposited mass.

Another conclusion can be done by observing the results from the the EIS. From Fig.3.48(b) all the three electrodes are similar from the resistive point of view while, regarding the capacitive behaviour, it decreases by increasing the Deposition Current.

All the parameters extracted from the electrochemical analysis of this test are reported in Table 3.14. The value of the sample corresponding to the process parameters $J_{DEP} = 1 \text{ mA cm}^{-2}$ and $t_{DEP} = 20 \text{ min are in the last raw and they}$ have been computed as a mean value of the three samples of Tests 1.

\mathbf{J}_{DEP}	\mathbf{t}_{DEP}	$\Delta \mathbf{m}$	Capac	itance	ESR	k (Ω)
$mAcm^{-2}$	min	mg	mFcm ^{-2}	Fg^{-1}	Before CV	After CV
0.1	200	0.052	63.72	612.72	9.587	7.919
0.5	40	0.132	72.95	276.32	6.371	5.258
1.0	20	1.171	119.21	53.29	7.588	6.558

Table 3.14: Electrode Parameters - FeO (TEST 2)

Test 3 - Electrolyte. Finally, in order to select the best electrolyte for the final device, FeO electrodes have been also studied in Li_2SO_4 0.5 M and K_2SO_4 0.5 M. Other two electrodes have been synthesized by applying electroplating for this final test.



Figure 3.49: EC Characterizations - FeO (TEST 3). (a) Electrolytes: Li_2SO_4 0.5 M, K_2SO_4 0.5 M, CV plots (b) Electrolytes: Li_2SO_4 0.5 M, Nyquist plot

The CV characterization have been performed at 1 mVs⁻¹ in this case in order to perform a comparison with the MnO electrodes in the by modifying the electrolyte. The other parameters are the same: 110 cycles and 1.1 V as Voltage Window. The CV plots are similar for the two cases.

Fig.3.49(b) shows the results from the Spectroscopy in the case of Li_2SO_4 0.5 M electrolyte. The behaviour is the same of the previous tests: after the CV cycles the real part and the negative imaginary part of the impedance became lower, and so, the electrode is less resistive and more capacitive.

Electrolyte	$\Delta \mathbf{m}$	Capac	ESR	
	mg	mFcm ⁻²	Fg^{-1}	Ω
$\begin{array}{c c} \text{Li}_2\text{SO}_4 \ 0.5 \text{ M} \\ \text{K}_2\text{SO}_4 \ 0.5 \text{ M} \end{array}$	$\begin{array}{c} 1.034 \\ 1.08 \end{array}$	296.94 303.45	$143.59 \\ 140.49$	$6.632 \\ 7.031$

Table 3.15: Electrode Parameters - FeO (TEST 3)

As usual, the Active Area is the same for both the electrodes and the electrolyte's concentration (0.5 M) has been omitted in the first column of Table 3.15. The ESR has been evaluated after CV.

From this study it is possible to conclude that by immersing the electrodes in these two electrolytes, the electrochemical parameters are comparable.



3.2 Device Fabrication

The two electrodes have been studied and optimized separately. They are now ready to be assembled to build up the final asymmetric device discussed in Section 1.2.

3.2.1 CAD Design and LIG process

As for the single electrodes case, the first task is the definition of the geometry to be transferred onto the kapton flexible substrate through DLW. The device will be planar (both cathode and anode will be printed on the same plane in a single step).

This geometry is more complex than that seen in the previous chapters and therefore was created using CAD software called *Rhinoceros*. The Active Area is the same for the 2 electrodes: a 1 cm^2 rectangular shape. Larger features have been printed to attach the current collector. Fig.3.50 shows the Rhinoceros' interface and the 2D CAD design of the device with all the quotes of interest.

The distance between the electrodes has been identified as d. Several prints have been made by modifying this parameter $d = \{300, 400, 500\} \mu m$, in order to see if it to see if has any influence on capacitive performance.

At the moment, interdigitated geometries have been printed but have not been synthesized and characterized because the TMOs depositions were not as expected.



Figure 3.50: Rectangular geometry - CAD design with Rhinoceros

The applied laser parameters are the same described in Section 3.1 and the output of the Laser Writing is reported in Fig.3.51.





Figure 3.51: LIG - Planar device geometry

These samples are now ready to be prepared for the electroplating: Ti grid will be applied to the larger LIG rectangular features through kapton scotch and only the two rectangular Active Areas will be left uncovered.



Figure 3.52: Preparation of the device for the electroplating process on both the electrodes. Cross section of all the steps (left) and example of two samples (right)

As can be seen from Fig.3.52 (right picture), current collectors have been labelled with a + or - in order to recognize the Metal Oxide to be deposited. Then, other two numbers have been written on the polymide: the first one is to identify the d parameter (300, 400 or 500) and the second one is to specify the sample, since 3 devices will be synthesized and studied for each d (1, 2 or 3).

So, each device can be identify with the symbol $D_{i,j}$, where the index j represent the d parameter and i is the sample index.


3.2.2 Charge Balancing

Before starting the electroplating procedure, it is important to have an idea of the amount of material that has to be deposited on each electrodes in order to respect the Charge Balancing of the device.

The condition to be satisfied is:

$$m_{-}Q_{-} = m_{+}Q_{+} \tag{3.10}$$

where m_- and m_+ are the masses of deposited FeO and MnO respectively, while Q_- and Q_+ are the charge stored at each electrode's interface. By using Eq.2.15, and by substituting the subscripts - and + with FeO and MnO, the previous expression can be written as:

$$m_{FeO}C_{FeO}V_{FeO} = m_{MnO}C_{MnO}V_{MnO} \tag{3.11}$$

where V_k (k = FeO, MnO) is the potential applied to the electrodes during the CV characterization: 0.8 V for the MnO positive electrode and 1.1 V for the FeO negative one. The capacitances C_k have been extraced from the CV characterizations in Fig.3.53.



Figure 3.53: CV plots for Manganese Oxide and Iron Oxide electrodes characterized in aqueous electrolyte: Li_2SO_4 , 0.5 M

At the end, we obtain:

$$\frac{m_+}{m_-} = \frac{m_{MnO}}{m_{FeO}} \equiv m_{\pm} = 0.64 \tag{3.12}$$

Starting from Eq.3.10 and inserting the values of the capacitances and of the applied potential window for each electrode, we find the condition (Eq.3.12) to be satisfied during the deposition processes. In order to do this, the calibration lines of equations 3.1 and 3.9 were used.

3.2.3 Electroplating

Politecnico di Torino

The deposition process has been performed within the same experimental setup used for the single electrodes. Iron Oxide will be deposited at first, since its deposition rate is lower and then, by combining Eq.3.12 and 3.1, the deposition time t_{DEP} for the Manganese Oxide deposition is computed, in order to respect the Charge Balancing condition.

From the previous experiments, by applying a current density of 1 mA cm⁻² for $t_{DEP} = 20$ min, the amount of deposited FeO was around 1 mg. The MnO to be deposited is lower than the FeO and theoretically, by using the calibration Lines, there is no positive deposition time to deposit such a small amount of material.

To overcame this issue, the Iron Oxide deposition parameters were increased: $J_{DEP} = 3 \text{ mA cm}^{-2}$, $t_{DEP} = 30 \text{ min}$. As usual, at the end of the deposition time, the samples are removed from the solution and left to dry in a desiccator for at least 4 hours. The deposited mass is measured and then the Manganese Oxide deposition can start with the t_{DEP} computed from Eq.3.1. All these passages are schematized in the cross section of Fig.3.54.



Figure 3.54: Cross Section of the device during the FeO and MnO deposition

The results from the deposition on the nine LIG substrates are reported in Table 3.16. In the column corresponding to the quantity MnO_{th} there are the values of the amount of deposited material expected from the Charge Balancing condition and from the measured FeO mass, while in the MnO column there are the actual deposited MnO masses.

Finally, in the m_{\pm} column, the mass ratios values are reported for each device. In some cases this value is too far from the expected value, as for $D_{3,300\mu m}$, $D_{3,400\mu m}$ and $D_{3,500\mu m}$. They were therefore discarded for future analyses.



d [μ m]	Sample	FeO [mg]	MnO_{th} [mg]	MnO [mg]	m _±
300	1	2.182	1.396	3.329	1.52
	2	1.951	1.249	1.932	0.99
	3	1.526	0.977	3.248	2.12
400	1	2.164	1.385	1.675	0.77
	2	2.189	1.401	3.159	1.44
	3	2.212	1.416	3.649	1.64
500	1	2.678	1.714	1.872	0.70
	2	1.899	1.215	2.217	1.17
	3	1.531	0.979	2.573	1.68

Table 3.16: Device - Amount of deposited mass

 $\mu {\rm SCs}$

Chapter 4

Discussion

4.1 Device Characterization

A first rough characterization was done on a sandwich configuration of the device before starting the analysis on the pouch cells.

Sandwich Configuration. This characterization was carried out by building the electrochemical cell similarly to the one for the single electrode characterization: two electrodes in front of each other separated by the glass fiber and pressed through glass slides and rubber bands. The electrolyte is Li_2SO_4 0.5 M. This technique was performed in Full Cell configuration. The WE is the NaMnO anode of the device, while the CE is coincident with the RE and it is the FeO cathode.

The first test to be observed through this simple analysis was the measure of the OCP. We expected a negative value since, from the measurements done on the electrodes separately, we had: $OCP_{FeO} > OCP_{MnO}$. These plots are reported in Fig.4.1(a) and 4.1(b).



Figure 4.1: OCV Characterization - Sandwich Device: (+) LIG | MnO | 0.5 M Li₂SO₄ | FeO | LIG(-). (a) OCV of the WE and CE; (b) OCV of the device

After the OCV test, the device was studied by applying the GCD technique. Also in this case, the results will be plotted for the device and for the electrodes separately. A single Current Rate equal to $\pm 330 \ \mu\text{A cm}^{-2}$ was applied for 20 cycles.



Figure 4.2: GCD Characterization - Sandwich Device: (+) LIG | MnO | 0.5 M Li₂SO₄ | FeO | LIG(-). (a) WE and CE separately; (b) Device measurements

The quasi-linear behaviour of the voltage E_{we} - E_{ce} in Fig.4.2(b) confirms the pseudocapacitive behavior exhibited by the device. The small voltage drop between the end of the charge period and the beginning of the discharge one indicates that this configuration is characterized by a low ESR. This asymmetric device with these selected transition metal oxides deposited on the electrodes was brought up to 1.9 V.



Figure 4.3: GCD Characterization - Sandwich Device: (+) LIG | MnO | 0.5 M Li_2SO_4 | FeO | LIG(-). (a) Capacitance Retention; (b) Coulombic and Energy Efficiency

From this GCD characterization, the capacitance and the efficiencies were obtained for each cycles and they are reported in Fig.4.3(a) and 4.3(b). The values

of the capacitance is low because the overall capacitance is dominated by the iron oxide electrode.

Pouch cell Configuration. The fabrication procedure of these devices was reported in Section 3.2.3. CV and EIS characterization were done on the samples $D_{1,300\mu m}$, $D_{1,400\mu m}$ and $D_{1,500\mu m}$. The results are reported in Fig.4.4 and Fig.4.6. Their deposition parameters, such as the mass loading for each electrode and the mass ratio, are reported in Table 3.16. This characterization was done at 10 mVs⁻¹ up to 1.9 V vs RE, for 100 cycles during which, as it can be observed from Fig.4.5(b), the Coulombic Efficiency is high.



Figure 4.4: CV plots - Devices in Pouch Cell Configuration



Figure 4.5: CV Characterization: Capacitance retention and efficiencies - Device $D_{1,500\mu m}$: (+) LIG | MnO | 0.5 M Li₂SO₄ | FeO | LIG(-)



From the CV plot in Fig.4.4 it is possible to say that no peaks appear due to unwanted phenomena at the electrolyte-electrodes interface, and so it possible to conclude that this μ SC was optimized to work up to 1.9 V.



Figure 4.6: Nyquist plots - Device in Pouch Cell Configuration

The Nyquist plots in Fig.4.6 represent the impedances of the two separated electrodes (dashed lines) and of the device (solid line). From this graph it can be seen how the impedance of the device is strongly dominated by the iron oxide counter electrode.

Device	\mathbf{m}_{\pm}	Capacitance		ESR (Ω)	
		mFcm ⁻²	Fg^{-1}	Before CV	After CV
$D_{1,300\mu m}$	1.52	16.62	3.01	29.02	28.48
$D_{1,400\mu m}$	0.77	23.06	6.01	22.45	21.65
$D_{1,500\mu m}$	0.70	28.55	6.28	22.56	22.9

 Table 4.1: Device Parameters

From these measurements it is possible to observe a trend regarding the variation of the d parameter. In fact, from Table 4.1, it is possible to observe how, by increasing the distance of the electrode printed onto the kapton substrate, the capacitance increases. Currently, there is no clear explanation for this evidence.

The same cell were also characterized through CDG investigating several current rates. The capacitance retention plot is reported in Fig.4.7(a), while the efficiencies are in Fig.4.8(a) and 4.8(b).



Figure 4.7: GCD Characterization - Pouch Cell Device: (+) LIG | MnO | 0.5 M Li_2SO_4 | FeO | LIG(-). Capacitance Retention



Figure 4.8: GCD Characterization - Pouch Cell Device: (+) LIG | MnO | 0.5 M Li₂SO₄ | FeO | LIG(-) (a) Coulombic Efficiency; (b) Energy Efficiency

From Fig.4.7(a) it is possible to observe that the Capacitance remains quite stable over the 100 cycles of each applied Current Rate during the CGD characterization and 4.7(b) confirms the fact that the Capacitance is higher by increasing the parameter d. This is an important result but it could be useful to apply the same characterization for more cycles to to draw conclusions about the ciclability of this μ SC.

The measured coulombic efficiency, shown in Fig.4.8(a), was very high during the entire measurement and so, at each current rate. Fig.4.8(b) illustrates instead the energy efficiency: as the current rate in increases, various sources of resistance and energy losses become more pronounced. These factors collectively lead to reduced this parameter.

4.2 Comparison with Literature

Politecnico di Torino

Graphene supercapacitors are quickly progressing from lab prototypes to potential rivals for commercial batteries. Their improved properties and performance over the last decade can be attributed to three key technologies [38]: graphene foam, laser reduction, and microsupercapacitors. Graphene foam, made via CVD with sacrificial templates, produces high-capacity electrodes for large supercapacitors. These electrodes have shown a gravimetric capacitance of up to 2585 F g⁻¹ and retain 96.5% capacitance after 10.000 cycles. Graphene's conductivity and porous structure enable lightweight and flexible 3D electrodes. DLW offers a cost-effective method for creating large, flexible electrodes using laser-reduced graphene oxide (LrGO) or LIG. Although DLW achieves good capacitance from CVD remains a challenge.



Figure 4.9: A real Ragone plot for graphene's electrodes used in μ SCs by using Laser and Non-Laser technologies

Fig.4.9 was obtained was obtained by rearranging the data found in Ref.[38].

These graphene forms offer functionalizable empty pore areas. μ SCs are gaining popularity for their integration into wearable electronics. Scaling down supercapacitor technology to the microscale offers advantages like improved power performance. Interdigitated Electrodes (IDEs) enhance ion accessibility, while gel and solid-state electrolytes allow easy integration into flexible modules. Portable, flexible and even wearable electronic devices have attracted great attention and may lead the next revolution in the field of electronics. [33] A number of new products or prototypes such as flexible displays, curved mobile phones, and electronic clothing, represent a new technological frontier. Flexibility is ideal for wearable electronics, where μ SCs are expected to play a crucial role.



Figure 4.10: Areal Ragone plot for a cellular graphene based μ SC and a quasi-solidstate μ SC in comparison with μ SCs based on different types of active materials, including laser reduced graphene, graphene quantum dots, reduced GO/CNT, thermally reduced graphene, vertically aligned graphene, graphene/phosphorene hybrid films, photochemically reduced graphene, S-doped graphene film, laserprocessed graphene and CVD graphene/CNT carpets hybrid materials

3D cellular graphene films [33] were fabricated by a freeze-casting assisted filtration assembly method showing great mechanical strength and flexibility. they were used as electrodes in quasi-solid-state μ SCs by using and polyvinyl alcohol (PVA)/H₃PO₄ as a gel electrolyte. It was used since electrolyte leakage is one of the main concerns when the μ SC is operated during bending. In comparison to a liquid electrolyte, solid-state electrodes can efficiently avoid the leakage problem, and



therefore reduce safety issues and the cost of device packaging. In addition, a solidstate electrolyte is easier to handle, and has greater reliability and a wider operating temperature range. This device demonstrates an impressive 97.6% capacitance retention after 10,000 continuous cycles. This level of performance is comparable with a graphene quantum dot-based μ SC [20] (97.8% retention after 5000 cycles) and surpasses the 96.5% retention after 10.000 cycles of laser-scribed graphene electrochemical capacitors and the 95% retention after 1000 cycles of rGO - CNT hybrid μ SC [5].

The Ragone plot of this cellular graphene based μ SC in comparison with other graphene based devices is reported in Fig.4.10, obtained using the data in Ref.[24]. It exhibits notable energy and power densities. In an aqueous electrolyte, they achieve an energy density of 0.34 mWh cm⁻² and a power density of 5.3 mW cm⁻². In a gel electrolyte, these values are 0.22 mWh cm⁻² for energy density and 0.37 mW cm⁻² for power density. These performances are comparable to μ SCs made from CVD 3D graphene/CNT carpets [19], graphene quantum dots in an organic electrolyte, 3D porous graphene [47], and outperform other μ SCs based on onion-like carbon [28], laser-reduced graphene [9], S-doped graphene film [41], and photochemically reduced graphene [40].



Figure 4.11: A real Ragone plot for LIG|FeOOH//LIG|MnO_2, LIG|MnO_2-2.5h and LIG |PANI-15

 μSCs

Pseudocapacitance was studied by Tour [18] by combining LIG with electrodeposition, flexible all solid state μ SCs with enhanced electrochemical performance are created. LIG acts as both an EDLC electrode and a conductive matrix for pseudocapacitive materials like manganese dioxide (MnO₂), ferric oxyhydroxide (FeOOH), and a conductive polymer called polyaniline (PANI). These materials are used to form LIG|MnO₂, LIG|FeOOH, and LIG|PANI composites, which are then employed in the assembly of all-solid-state, flexible symmetric and asymmetric μ SC with IDEs. These devices offer energy densities comparable to microbatteries, excellent rate performance, cycling stability, and mechanical flexibility without the need for current collectors, binders, or separators. The thickness of these electrodeposited pseudocapacitive materials was extrapolated from the plots in Ref.[18]: t_{FeOOH//MnO2} = 231 μ m, t_{MnO2-2.5h} = 327 μ m and finally t_{PANI-15} = 76 μ m.

A comparison between these devices and the asymmetric device of this work is reported in Fig.4.11, where the plots and curves were obtained through the data in Ref.[18]. The asymmetric device synthesized and discussed in Ref.[18] presents better performances than the one created in this work. This difference could be sought in the quality of the iron oxide obtained, and therefore in the method of synthesis of the latter. Tour deposited FeOOH onto LIG by mounting a two electrode cell with a 0.1M FeCl₃ solution and by applying a constant current density of 15 mA cm⁻² and by varying the deposition time to monitoring the amount of obtained material. Regarding the areal capacitance, at 0.5 mA cm⁻² the asymmetric device in this work reaches 27.46 mF cm⁻², while the asymmetric μ SC discussed in [18] is 20.56 mF cm⁻².

4.3 Conclusions

The energy and power densities obtained for the μ SC of this work are comparable with the results in the Ragone plots found in literature for most graphene's electrodes based microsupercapacitors discussed before in Fig.4.9, electrodes made of several carbonaceous materials in 4.10 and electrode coated by transition metal oxides.

This confirms the goodness of the use of laser writing to obtain graphene's substrates for the deposition of metal oxides such as pseudocapacitive materials, within an asymmetric μ SC with aqueous electrolyte.

The XPS characterization showed that the synthesized manganese oxide thin film is composed by a mixture of Mn(III) and Mn(IV), which faradaic reactions with the electrolyte's ions provide an electrode areal capacitance equal to 249.583 mF cm⁻² for the Li-MnO, 287.815 mF cm⁻² for the Na-MnO and 330.098 mF cm⁻² for the K-MnO. So, the variation of the support salt in the electroplating solution can be a good design parameter to improve the capacitive performances. Furthermore, self discharge can be limited by removing O₂ molecules from the μ SC's atmosphere.

The iron oxide cathode deposited onto the LIG through the electroplating reaches an areal capacitance equal to 119.21 mF cm⁻², but the Spectroscopies carried out on this electrodes shows a much more resistive behaviour with respect to the anode. This property of the negative electrode has a great impact on the final device which is equally resistive. In any case, the voltage of the device assembled as explained can be brought up to 1.9 V, which is a higher value with respect to the aqueous electrolyte based device.

The device's performances regarding the energy and power capabilities are illustrated in the Ragone plots in Fig.4.9, 4.10 and 4.11. Although the results are comparable with those of electrodes synthesized with carbonaceous materials, they are still inferior to those of asymmetric devices with the same pseudocapacitive materials found in the literature. It could be attributed to the quality of the deposited metal oxides thin films. On the other hand, however, the advantage of the asymmetric device created in this work is the very simple manufacturing process compared to those discussed in the literature.

It will be important to perform new tests on the device to test its cyclability over a much larger number of cycles than that discussed in the previous paragraphs.

Improvements in the final performances can be done by optimizing the iron oxide electrode even further, (a) by recognize the stoichiometry of the deposited FeO_x through XPS, XRD or Raman analysis and obtain new process parameters to improve the deposition efficiency computed with the Faraday's law; (b) by investigating other Transition Metal Oxides that can be used as negative electrode.

The applications of micro supercapacitors are continuously expanding due to their small size, rapid charge/discharge capabilities, and long lifespan. They are often used in combination with other power sources, by integrating them with microbatteries or solar panels, to improve energy efficiency in devices and systems. They can be also used particularly in wearable and flexible electronics due to their flexibility coming from the kapton, LIG and metal oxides properties.

 μSCs

Appendix

MATLAB Codes

Amount of deposited mass

The MATLAB code used to evaluate the amount of deposited material Δm for each sample after the electroplating process is reported here.

```
close all; clear all; clc;
```

```
N = 3; % Number of Samples
%% Data Import - Mass before Deposition
sam1 = readmatrix('Sample1_massa_before_dep.txt');
sam2 = readmatrix('Sample2_massa_before_dep.txt');
sam3 = readmatrix('Sample3_massa_before_dep.txt');
% L: Length of the imported File - Number of measurements on
% the single sample
L = length(sam1);
% N x L Matrix: sam (variable name)
% N: Number of Samples
% L: Number of mass measuremnts
sam = zeros(N,L);
sam(1,:) = sam1;
sam(2,:) = sam2;
sam(3,:) = sam3;
% Standard Deviation and Mean Value calculation for each sample
% Variables Initialization
std = zeros(N, 1)
mean_val = zeros(N,1);
% Computation
[std(1),mean_val(1)] = std(sam(1,:));
[std(2),mean_val(2)] = std(sam(2,:));
[std(3),mean_val(3)] = std(sam(3,:));
```

APPENDIX

```
% Display Results of the Mass for each sample on the Command Window
format long
disp('ELECTROPLATING')
disp('Process Parameters:')
disp('- Deposition Current: JDEP mAcm-2')
disp('- Deposition Time: tDEP min')
disp(' ')
disp('MASS MEASUREMENTS:')
disp('-----')
disp('- Mass of the Samples BEFORE Deposition:')
disp(['m1 = (',num2str(mean_val(1)),' +/- ',num2str(std(1)),') g'])
disp(['m2 = (',num2str(mean_val(2)),' +/- ',num2str(std(2)),') g'])
disp(['m3 = (',num2str(mean_val(3)),' +/- ',num2str(std(3)),') g'])
disp(' ')
%% Data Import - Mass after Deposition
sam1_dep = readmatrix('Sample1_massa_after_dep.txt');
sam2_dep = readmatrix('Sample2_massa_after_dep.txt');
sam3_dep = readmatrix('Sample3_massa_after_dep.txt');
% L_dep: Length of the imported File - Number of measurements on
% the single sample
L_dep = length(sam1_dep);
% N x L_dep Matrix: sam_dep
% N: Number of Samples
% L_dep: Number of mass measuremnts
sam_dep = zeros(N,L_dep);
sam_dep(1,:) = sam1_dep;
sam_dep(2,:) = sam2_dep;
sam_dep(3,:) = sam3_dep;
% Standard Deviation and Mean Value calculation for each sample
% Initialization
std_dep = zeros(N,1)
mean_val_dep = zeros(N,1);
% Computation
[std_dep(1),mean_val_dep(1)] = std(sam_dep(1,:));
[std_dep(2),mean_val_dep(2)] = std(sam_dep(2,:));
[std_dep(3),mean_val_dep(3)] = std(sam_dep(3,:));
```

% Display Results of the Mass for each sample on the Command Window format long

Up to now it was just a matter of data import and Mean Value and Standard Deviation computation for the electrodes before and after the process.

Starting from the following lines, the Δm computation and the propagation of the Standard Deviation will be computed.

Finally, the message in the MATLAB Command Window will show the declaration of the results as reported in this example:

MASS MEASUREMENTS:



```
- Measurement Result Statement
SAMPLE 1: dm = 4.558 \text{ mg } +/- 0.13667 \text{ mg}
SAMPLE 2: dm = 1.876 \text{ mg } +/- 0.1145 \text{ mg}
```

```
SAMPLE 3: dm = 2.527 mg +/- 0.12362 mg
```

CV Cycles

The MATLAB code used to evaluate the Capacitance Retention and the behaviour of other quantities obtained through the CV characterization as a function of the cycles is reported here.

```
close all; clear all; clc;
%% Data Import
file = readmatrix('____.txt');
% Length of the file: number of points for each measured quantity
L = length(file);
time = file(:,1);
                % Time, s
Ewe = file(:,2);
                 % Potential vs Ag/AgCl, V
I = file(:,3);
                 % Current, mA
               % Cycle Number
cyc = file(:,4);
time = time - time(1); % The time variable starts from 0 s
%% Data Elaboration
N = cyc(end);
                    % Number of cycles
single_cyc = zeros(N,1); % This array contains the number
                    % of points for each cycle
% Find the number of points for each cycle
i = 1;
for ind = 1:L
   if cyc(ind) == i
      single_cyc(i,1) = single_cyc(i,1) + 1;
   else
      i = i + 1;
   end
end
```

```
% Variables Iniziatization
for j = 1:length(single_cyc)
    Voltage = zeros(single_cyc(j),length(single_cyc));
    Current = zeros(single_cyc(j),length(single_cyc));
    DeltaT = zeros(single_cyc(j),length(single_cyc));
end
% Variable Assignment
sum = 0;
for j = 1:N
    for k = 1:single_cyc(j)
        if (j == 1)
            Voltage(k,j) = Ewe(k);
            Current(k,j) = I(k);
            DeltaT(k,j) = time(k);
        end
        if (j > 1)
            Voltage(k,j) = Ewe(k + sum - 1);
            Current(k, j) = I(k + sum - 1);
            DeltaT(k,j) = time(k + sum - 1);
        end
    end
    sum = sum + single_cyc(j);
end
% Electrode Parameters
dm = ____;
                % Deposited mass, g
                % Active Area, cm<sup>2</sup>
area = ___;
% Initialization of the quantities from CV
q_dis = zeros(N,1);
                      % Discharge Capacity, mC
q_ch = zeros(N,1);
                      % Charge Capacity, mC
                      % Discharge Energy Density, Wh
E_dis = zeros(N,1);
E_ch = zeros(N,1);
                      % Charge Energy Density, Wh
eta_C = zeros(N,1); % Coulombic Efficiency
eta_E = zeros(N,1); % Energy Efficiency
```

Now a loop over each cycle will start, and all the desired quantities will be computed and stored into the previously initialized arrays, separating the charge and the discharge phase for each cycle, in order to evaluate the efficiencies.

```
for ind = 1:N
    [m,pos] = max(Voltage(:,ind));
                                         % End of the charge phase:
                                         % m: Max Potential Value
                                         % pos: index corresponding to m
    % Discharge Current, mA
    curr_dis = Current([pos:min(single_cyc)],ind);
    % Charge Current, mA
    curr_ch = Current([1:pos],ind);
    dt = DeltaT([pos:min(single_cyc)],ind);
                                              % Discharge Time, s
    deltat_dis = dt(end) - dt(1);
    dt = dt - dt(1);
    dt_ch = DeltaT([1:pos],ind);
                                               % Charge Time, s
    deltat_ch = dt_ch(end) - dt_ch(1);
    dt_ch = dt_ch - dt_ch(1);
    dV = Voltage(pos,j) - Voltage(1,j);
                                         % Applied Potential Window, V
    % Absolute Value of the Charge and Discharge Currents
    % to compute the integral
    curr_dis = abs(curr_dis);
    curr_ch = abs(curr_ch);
    % Discharge Phase
    q_dis(ind,1) = trapz(dt_dis,curr_dis);
                                            % Discharge Capacity, mC
    dV = Voltage(pos,j) - Voltage(1,j);
                                             % Voltage Window, V
    C = q/dV;
                                             % Capacitance, mF
    C_{mass} = C/(1000*dm);
                                             % Capacitance, F/g
    C_area = C/area;
                                             % Capacitance, mF/cm<sup>2</sup>
    E_{dis} = (C.*dV^2)/2;
                                             % Discharge Energy, Wh
    % Charge Phase
    q_ch(ind,1) = trapz(dt_ch,curr_ch);
                                            % Charge Capacity, mC
    C_ch = q_ch/dV;
                                             % Charge Capacitance, mF
    E_ch = (C_ch.*dV^2)/2;
                                             % Charge Energy, Wh
    % Coulombic Efficiency
    eta(ind,1) = q_dis(ind,1)/q_ch(ind,1);
    % Energy Efficiency
    eta_E(ind,1) = abs(E_dis(ind,1))/abs(E_ch(ind,1));
end
```

Once all the quantities have been computed for each cycle, they are ready to be plotted. Only the commands for the Capacitance Retention Plot has been reported.



•

```
% Plot of the Capacitance Retention
figure(1)
hold on
box on
plot(cycle,C,'b-o','LineWidth',1.5)
xlabel('cycle number')
ylabel('C [mF]')
title('Capacitance vs. Cycle Number')
```

Bibliography

- Andreas et al. Self-discharge in manganese oxide electrochemical capacitor electrodes in aqueous electrolytes with comparisons to faradaic and charge redistribution models. *Electrochimica Acta*, 140:116–124, 2014.
- [2] Andreas et al. Self-discharge in electrochemical capacitors: a perspective article. Journal of The Electrochemical Society, 162(5):A5047, 2015.
- [3] Ardizzone et al. Mn3o4 and γ-mnooh powders, preparation, phase composition and xps characterisation. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 134(3):305–312, 1998.
- [4] J. Balmer. Lecture notes, universitat bern. *Festkorperphysik*, 2010.
- [5] Beidaghi et al. Micro-supercapacitors based on interdigital electrodes of reduced graphene oxide and carbon nanotube composites with ultrahigh power handling performance. Advanced Functional Materials, 22(21):4501–4510, 2012.
- [6] Bryan et al. Conducting polymers for pseudocapacitive energy storage. Chemistry of Materials, 28(17):5989–5998, 2016.
- [7] Cui et al. Revealing pseudocapacitive mechanisms of metal dichalcogenide sns2/graphene-cnt aerogels for high-energy na hybrid capacitors. Advanced Energy Materials, 8(10):1702488, 2018.
- [8] Ding et al. Metallic mesoporous nanocomposites for electrocatalysis. *Journal* of the American Chemical Society, 126(22):6876–6877, 2004.
- [9] Gao et al. L., ci, r. vajtai, q. zhang, b. wei, and pm ajayan, â. Direct laser writing of micro-supercapacitors on hydrated graphite oxide films, â Nat. Nanotechnol, 6:496-500, 2011.

- [10] Huang et al. Origin of superior pseudocapacitive mechanism of transition metal nitrides. Journal of Energy Chemistry, 69:561–568, 2022.
- [11] Gregory Jerkiewicz. Applicability of platinum as a counter-electrode material in electrocatalysis research. ACS Catalysis, 12(4):2661–2670, 2022.
- [12] Jiang et al. Definitions of pseudocapacitive materials: a brief review. Energy & Environmental Materials, 2(1):30–37, 2019.
- [13] Kalantar-Zadeh et al. Two dimensional and layered transition metal oxides. Applied Materials Today, 5:73–89, 2016.
- [14] Lamberti et al. New insights on laser-induced graphene electrodes for flexible supercapacitors: tunable morphology and physical properties. *Nanotechnology*, 28(17):174002, 2017.
- [15] James Larminie, Andrew Dicks, and Maurice S McDonald. Fuel cell systems explained, volume 2. J. Wiley Chichester, UK, 2003.
- [16] Le et al. Recent advances in laser-induced graphene: Mechanism, fabrication, properties, and applications in flexible electronics. 32(48):2205158, 2022.
- [17] Lherbier et al. Transport properties of graphene containing structural defects. *Physical Review B*, 86(7):075402, 2012.
- [18] Li et al. High-performance pseudocapacitive microsupercapacitors from laserinduced graphene. Advanced Materials (Deerfield Beach, Fla.), 28(5):838–845, 2015.
- [19] Lin et al. 3-dimensional graphene carbon nanotube carpet-based microsupercapacitors with high electrochemical performance. Nano letters, 13(1):72–78, 2013.
- [20] Liu et al. Superior micro-supercapacitors based on graphene quantum dots. Advanced Functional Materials, 23(33):4111–4122, 2013.
- [21] Liu et al. Iron oxide/oxyhydroxide decorated graphene oxides for oxygen reduction reaction catalysis: a comparison study. *RSC advances*, 6(35):29848– 29854, 2016.
- [22] H. Luth. Solid Surfaces, Interfaces and Thin Films, Springer-Verlag:(sec. 6.3, Panel XI), 2010.

- [23] Lv et al. Progress in iron oxides based nanostructures for applications in energy storage. Nanoscale Research Letters, 16(1):138, 2021.
- [24] Meng et al. High-performance all-carbon yarn micro-supercapacitor for an integrated energy system. Advanced Materials, 26(24):4100–4106, 2014.
- [25] N. D. Mermin N. W. Ashcroft. Solid state physics. 1976.
- [26] Niu et al. In-situ growth of homogeneous δ-mno2 within lignin based porous carbon to reassemble uniform mesoporous crosslinked 3d-network structure for supercapacitors. *Materials Chemistry and Physics*, 305:127941, 2023.
- [27] Oickle et al. Examination of water electrolysis and oxygen reduction as selfdischarge mechanisms for carbon-based, aqueous electrolyte electrochemical capacitors. The Journal of Physical Chemistry C, 115(10):4283–4288, 2011.
- [28] D Pech. M. brunet, h. durou, p. huang, v. mochalin, y. gogotsi, p.-l. taberna, p. simon. Nat. Nanotechnol, 5:65, 2010.
- [29] NMR Peres. The transport properties of graphene. Journal of Physics: Condensed Matter, 21(32):323201, 2009.
- [30] Nuno MR Peres. Colloquium: The transport properties of graphene: An introduction. *Reviews of modern physics*, 82(3):2673, 2010.
- [31] Rao et al. Transition metal oxides. Annual Review of Physical Chemistry, 40(1):291–326, 1989.
- [32] Reina et al. Decoration of laser induced graphene with mxene and manganese oxide for fabrication of a hybrid supercapacitor. *Electrochimica Acta*, page 143163, 2023.
- [33] Shao et al. Flexible quasi-solid-state planar micro-supercapacitor based on cellular graphene films. *Materials Horizons*, 4(6):1145–1150, 2017.
- [34] Sun et al. Controlled synthesis of nanostructured manganese oxide: crystalline evolution and catalytic activities. *CrystEngComm*, 15(35):7010–7018, 2013.
- [35] Taberna et al. Electrochemical characteristics and impedance spectroscopy studies of carbon-carbon supercapacitors. *Journal of the Electrochemical Society*, 150(3):A292, 2003.

- [36] Tanaka et al. A review on iron oxide-based nanoarchitectures for biomedical, energy storage, and environmental applications. *Small Methods*, 3(5):1800512, 2019.
- [37] Trasatti et al. Electrochemistry and environment: the role of electrocatalysis. International journal of hydrogen energy, 20(10):835–844, 1995.
- [38] Velasco et al. Recent trends in graphene supercapacitors: from large area to microsupercapacitors. Sustainable Energy & Fuels, 5(5):1235–1254, 2021.
- [39] Wang et al. Dispersing pt atoms onto nanoporous gold for high performance direct formic acid fuel cells. *Chemical Science*, 5(1):403–409, 2014.
- [40] Wang et al. Scalable fabrication of photochemically reduced graphene-based monolithic micro-supercapacitors with superior energy and power densities. ACS nano, 11(4):4283–4291, 2017.
- [41] Wu et al. Bottom-up fabrication of sulfur-doped graphene films derived from sulfur-annulated nanographene for ultrahigh volumetric capacitance microsupercapacitors. Journal of the American Chemical Society, 139(12):4506–4512, 2017.
- [42] Xie et al. Ultrafine-mn2o3@ n-doped porous carbon hybrids derived from mnmofs: Dual-reaction centre catalyst with singlet oxygen-dominant oxidation process. *Chemical Engineering Journal*, 429:132299, 2022.
- [43] Xu et al. A rechargeable aqueous zinc/sodium manganese oxides battery with robust performance enabled by na2so4 electrolyte additive. *Energy Storage Materials*, 38:299–308, 2021.
- [44] Yi et al. Recent advances in pseudocapacitor electrode materials: transition metal oxides and nitrides. Transactions of Nonferrous Metals Society of China, 28(10):1980–2001, 2018.
- [45] Zeng et al. Electrodeposition of hierarchical manganese oxide on metal nanoparticles decorated nanoporous gold with enhanced supercapacitor performance. 632:376–385, 2015.
- [46] Zhang et al. Supercapacitors performance evaluation. Advanced Energy Materials, 5(6):1401401, 2015.



- [47] Zhang et al. Flexible micro-supercapacitor based on graphene with 3d structure. Small, 13(10):1603114, 2017.
- [48] Klaus Ziegler. Robust transport properties in graphene. *Physical review letters*, 97(26):266802, 2006.

Ringraziamenti

Un autentico grazie al prof. Lamberti, per avermi dato la possibilitá di entrare a far parte di questo progetto ed essere stato disponibile dal primo giorno. Un ringraziamento speciale va a Pietro Zaccagnini e Marco Reina per avermi guidato in questa esperienza completamente nuova e per le risposte a tutte le mie numerosissime domande in questi mesi di lavoro.

Grazie a Torino, per aver messo in chiaro le cose fin da subito, perché il tuo cielo sempre grigio e cupo, che mi ricordava ogni giorno che ero lí per diventare, da ragazzino, uomo. Quante volte l'ho guardato e ci ho visto un aereo, e quante volte ho sperato che fosse il mio per tornare a casa. Per questo, grazie per avermi fatto capire che quell'aereo me lo sarei dovuto guadagnare studiando e migliorandomi ogni giorno, con costanza e determinazione. Soprattutto, grazie perché quando il grigio veniva spazzato via dal sole, diventavi la cittá piú bella del mondo: la mia seconda casa per 5 lunghi anni. Il mio cuore conserverá per sempre un posto riservato a te.

Grazie a Taranto, per non avermi mai fatto sentire in colpa per essere andato via e anzi, grazie perché ogni volta che guardavo il mare del porto mercantile prima di salire sul pullman per Torino, nel rumore delle onde sentivo sempre un "In bocca al lupo, sono fiero di te, ce la farai". Dopo 20 anni in una cittá pensi di conoscerla bene, ma non mi ero mai reso conto come in questi 5 anni, di quanto fossero buone le pettole la mattina del 22 novembre. Lo sai quanto vorrei essere tuo ospite per sempre e lo so anche io quanto allo stesso modo vorresti ospitarmi e per questo grazie, perché le tue onde non smettono mai di fare rumore. Ti prometto che non ti deluderó e che continuerai ad essere sempre di piú fiera di me.

Grazie ai miei genitori, banalmente per il supporto costante che mi avete fatto sentire ogni giorno di questo viaggio lontano da casa. Grazie per avermi sempre spianato la strada, facendomi sentire protetto davanti alle difficoltá, rendendomi piú semplice tappa della mia vita, ma soprattutto facendomi capire, attraverso gesti, parole e scelte, che nulla é dovuto o gratuito, e che tutto va guadagnato con sacrificio e passione. Grazie per avermi insegnato l'importanza di viaggiare e quindi per avermi fatto crescere rispettoso e curioso di tutto ció che per me é una novitá.

Mamma, grazie per avermi insegnato ad affrontare ogni persona ed ogni situazione con gentilezza, educazione ed amore e per avermi insegnato ogni giorno il significato del verbo amare, mostrandomi la bellezza di donarsi senza limiti alle persone, anche se non ricambieranno o se dimenticheranno, perché il bene ti entra nel cuore e non va via.

Papá, grazie per essere sempre stato il mio scudo, il morbido cuscinetto dove poter cadere tranquillamente senza farsi male nonostante gli errori e le ingenuitá, in silenzio e senza mai prenderti meriti, e per questo, grazie per avermi insegnato l'umiltá. Ti ricordi quando la sera, dopo cena, mi prendevi in braccio per giocare a "Vola Vola il gabbiano" o quando l'estate mi insegnavi a tuffarmi in piscina dal trampolino? Ecco, ora quel bambino é arrivato qui e non vede l'ora di dimostrarti dove ancora puó arrivare: anche l'ambizione, me l'hai insegnata tu.

Grazie a Paola, la persona piú incredibile che abbia mai conosciuto. Quante volte in questi ultimi anni ho pensato che fosse tutto troppo difficile, ma poi prima dell'esame mi arrivava sempre il tuo messaggio da tifosa numero uno. Grazie per le passeggiate d'inverno sulla spiaggia, per i tragitti in macchina con la musica alta, per il volo dell'angelo e per il quad sul deserto. Grazie perché ogni volta, insieme a te, tutti i problemi sparivano e riuscivo a tornare sui libri piú forte di prima.

Grazie a tutti i miei nonni, a voi che siete qui e a quelli che non ci sono piú. Grazie per essere stati spettatori di questo percorso in punta di piedi per paura di distrarmi ed orgogliosi di qualsiasi passo avanti, sempre impazienti di vedermi tornare. Grazie a nonna Vanda e nonna Gianna, per avermi regalato l'arte delle vostre mani nei pranzi della domenica, determinate a prepararmi i piatti migliori del mondo anche a costo di non dormire la notte. Grazie a nonno Mimino, per la sua saggezza e la sua emozione, per i bar della mattina alle 10, per i bicchieri di vino versati di nascosto. Non avrei potuto concludere questo lungo viaggio senza la passione, l'impegno, la dedizione, l'ordine e la cura nello studio, e tutte queste qualitá le ho imparate piccolo: grazie a zia Ciretta per quegli indimenticabili 5 anni della scuola elementare.

Grazie a tutti i miei zii, per ogni incoraggiamento, parola di supporto, augurio prima e dopo un esame e per avermi dato la consapevolezza di non essere da solo quando ero triste prima di ripartire, durante tutti questi 5 anni. Grazie ai miei tre cugini per essere sempre stati con me nonostante la distanza. A Davide, per essere



stato il mio primo fratello maschio minore, per aver condiviso con me amicizie, passioni, viaggi, serate, sport. Concludere un percorso porta con se anche tanta malinconia: grazie ad Alessandro, per regalarmi ogni volta la possibilitá di tornare indietro nel tempo guardantoti e vedendo me con le emozioni e le paure dei primi giorni. Grazie a Carla, la piú piccola, per la tua costante allegria e la tua tua folle intraprendenza, e per avermi sempre fatto sentire importante ed un punto di riferimento.

A Silvia, da otto incredibili anni, la mia quotidianitá. Grazie per la tua presenza di ogni giorno e per i racconti, prima di addormentarci, dei nostri sogni, quelli vissuti e quelli che vorremmo vivere, ovviamente, insieme. Grazie per capire, senza chiedere, il mio stato d'animo e per avere la capacitá di farmi sorridere anche solo vedendoci la sera dopo una lunga e noiosa giornata. Grazie per essere sempre molto di piú di quello che merito, e soprattutto grazie per donarmi sempre tutta te stessa, senza mai pensare a ricevere nulla in cambio. Grazie a Ide, Enzo e Mirko, e a tutti i numerosissimi componenti della tua grande famiglia, per avermi sempre fatto sentire a casa.

Daniele e Danilo, grazie per avermi sempre fatto capire di non essere da solo, per i week end passati a scegliere cosa mangiare il sabato sera e la domenica a pranzo e per aver condiviso con me le esperienze migliori che potessi vivere. Grazie a Daniele per aver sempre fatto di tutto per convincermi di essere il migliore, per la tensione 90 minuti più recupero a settimana davanti alla televisione e per la fatica nel seguire la dieta. Grazie a Danilo, per non essersi mai stancato di coinvolgermi in qualunque cosa ti venisse in mente, per le trasferte di squadra e per i consigli informatici.

Succede sempre tutto cosí in fretta, un giorno finisci la scuola e l'altro ti ritrovi ad essere fuorisede dall'altra parte d'Italia. Grazie ad Angela e Alessandra perché, nonostante i tanti cambiamenti, siete state una costante che mi ha fatto sentire piú forte.

Grazie a Chiara e Ivan per essere stati, durante tutto questo percorso, sempre pronti a consigliarmi sulle scelte universitarie ed extra universitarie. Stasera festeggiamo, ma non dimentico che si avvicina quel tanto atteso momento in cui non sarete piú voi ad offrirmi al ristorante, ma io a voi. A Gianni e Grazia, da sempre presenti nella mia vita da quando ero solo un bambino. Grazie per le vostre canzoncine dopo ogni esame e la mattina del compleanno, e per i tantissimi bicchieri di amaro offerti alla villa.