



Università
di Catania

DOTTORATO DI RICERCA IN

SCIENZA DEI MATERIALI E NANOTECNOLOGIE – XXXVIII CICLO

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Molybdenum based nanostructures for energy production and storage

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TESI PER IL CONSEGUIMENTO DEL TITOLO DI DOTTORATO DI RICERCA

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Abstract

Abstract

The climate change experienced in recent decades demands new solutions for energy production and storage. In this view, the conversion of recycled industrial waste into efficient nanocatalysts offers an attractive pathway toward renewable and sustainable technologies.

Here, Mo-based industrial waste powders were transformed into three distinct nanostructured materials through cost-effective hydrothermal processes: MoO₃-nanobelts, MoS₂/MoO₃-nanostructures, and MoS₂-nanosheets. Phase and morphological characterizations were performed using Scanning Electron Microscopy, Transmission Electron Microscopy, X-Ray Diffraction, Raman Spectroscopy, UV-Vis Spectroscopy, X-Ray Photoelectron Spectroscopy, and X-Ray Absorption Spectroscopy.

The pH-controlled hydrothermal processing of Mo-based industrial waste powder leads to pure orthorhombic MoO₃ nanobelts (50-200 nm wide, 10 μ m long) with promising Oxygen Evolution Reaction (OER) performances at 10 mA cm⁻² with an overpotential of 324 mV and Tafel Slope of 45 mVdec⁻¹ in 1M KOH electrolyte. Then, MoO₃-nanobelts were sulfurized obtaining MoS₂/MoO₃ nanostructures through a hydrothermal process. Hydrogen Evolution Reaction (HER) measurements in 1M H₂SO₄ show a promising overpotential of 208 mV at 10 mA cm⁻² and a Tafel slope of 94 mV dec⁻¹. An overall water splitting cell was successfully assembled employing these materials, reaching a potential of 1.9 V.

Electrochemical studies on MoO₃-nanobelts in different alkaline electrolytes revealed distinct storage mechanisms. Capacitive and pseudocapacitive behaviours were evaluated in 1M KOH and 1M NH₄OH, respectively, using Cyclic Voltammogram (CV),

Abstract

Galvanostatic Charge-Discharge (GCD) and Electrochemical Impedance Spectroscopy (EIS) analyses.

Furthermore, MoS₂-nanosheets synthesised from recycled materials outstanding supercapacitor performance in 1M (NH₄)₂SO₄. They show a promising results reaching 1200 and 360 Fg⁻¹ at 5 mVs⁻¹ and 3Ag⁻¹, respectively from CV and GCD measurements. A coin cell device was fabricated from MoS₂-nanosheets, which works as a supercapacitor with promising also at higher current densities reaching 70 Fg⁻¹ at 10 Ag⁻¹.

This work highlights the great potential of upcycling industrial waste into high-performance nanocatalysts for both energy production and storage. Thus, bridging waste management with sustainable energy applications

Chapter 1. Energy management and sustainability

1.1 Energy storage systems: Challenges and perspectives

In 1799, Alessandro Volta, combining physics and chemistry, did one of the first registered experiments in electrochemistry; he built an electrochemical cell based on zinc and copper discs separated by a wet one [1]. This device (see **Figure 1a**) paved the way for both a new scientific field, which is the electrochemistry, and the development of modern society based on electricity. Indeed, electric energy found different employment in the last two centuries, which required a deeper understanding of the mechanisms and the study of more efficient solutions concerning the Volta cell.

Computer, smartphone and many other portable devices changed our life, this was possible thanks to Goodenough and colleagues, who are the fathers behind the modern Lithium-ion battery, still a device based on redox reactions which occur at the electrode interfaces [2]. The possibility to assemble portable electric devices thanks to Lithium-ion batteries (see **Figure 1b**) produced an extraordinary revolution in our daily life. Electric-based devices also improve our health care, as different studies showed, studying the difference between low- and middle-income countries and others in which access to energy facilities is easier [3]. Following, there is a discussion on the state-of-the-art and perspectives for the future of the field.

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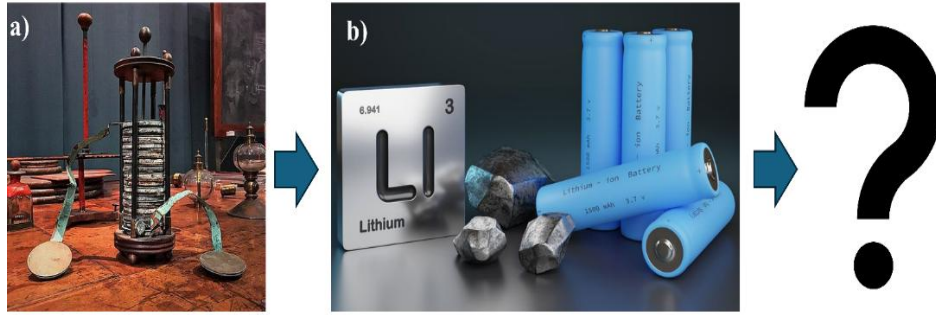


Figure 1 From the Volta cell (a), through modern Lithium-ion batteries (b).

As learned from what previously said, access to a secure electric facility is strongly connected to the economic growth of a country [4]. Unfortunately, energy sources have also several connected issues, indeed, greenhouse gases effects on the environment and human health have been well-known and widely studied in the last decades [5], [6]. In the last years, an increasing interest in clean energy sources has been registered, also due to the increase of extreme climate events; this new focus is represented by the increasing funding for renewables [7].

Renewable energy sources have bottlenecks linked to their storage systems, but in the last years different solutions have been proposed [8]. In particular, the employment of efficient energy storage systems (ESS) coupled with renewable energy reduces electricity use, enhancing efficiency and reliability of the system; and less carbon is produced in the global process, allowing also the distribution in isolated areas [9], [10]. Focusing on the ESS, there are several different types [11], with different mechanisms. For example, we can find the electric energy storage systems, which can be divided again into electrostatic and magnetic systems; capacitors and supercapacitors belong to the first type, both of which deal with charge stored in the metal electrode surface; the main difference between them is the energy density [12]. Superconducting magnetic energy storage (SMES) devices are based

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on magnetic mechanisms, but they require very low temperatures and high magnetic fields, increasing the cost of this technique [13], [14]. Different energy and power sources can also be employed to build hybrid systems; for example, these are used to drive vehicles [15]. Mechanical energy storage systems are one of the oldest techniques; in this case, the energy can be stored for long periods, and it is easy to convert [16]. Hydro, compressed air, flywheel and gravitational potential energy storage systems belong to this field. The energy can also be stored through the temperature thanks to thermal energy storage systems (TESS), which are composed of a heat storage tank, an energy transfer medium and a controlled system [9]. One of the most common systems is represented by the electrochemical energy storage systems (ECESS), lead acid and Lithium-ion batteries belong to this class of devices [9], [17], as just said they are strongly used for portable applications [9]. The last class of systems is the chemical energy storage systems (CESSs); here, chemical bonds are broken, and the formation of new ones is observed [11]. There are different types of CESSs, depending on the ions involved for the storage, there is the possibility to store hydrogen, but it is not stable at room temperature, for this and other reasons many scientists propose also ammonia storage which has a higher overall energy efficiency than hydrogen storage and other techniques, and it works at room temperature in liquid form [18]. Today, new hybrid devices which merge different classes of ESSs are evaluated to achieve the energy requirements of consumers, also taking into account of the chosen materials to increase features like lifespan and efficiency [19].

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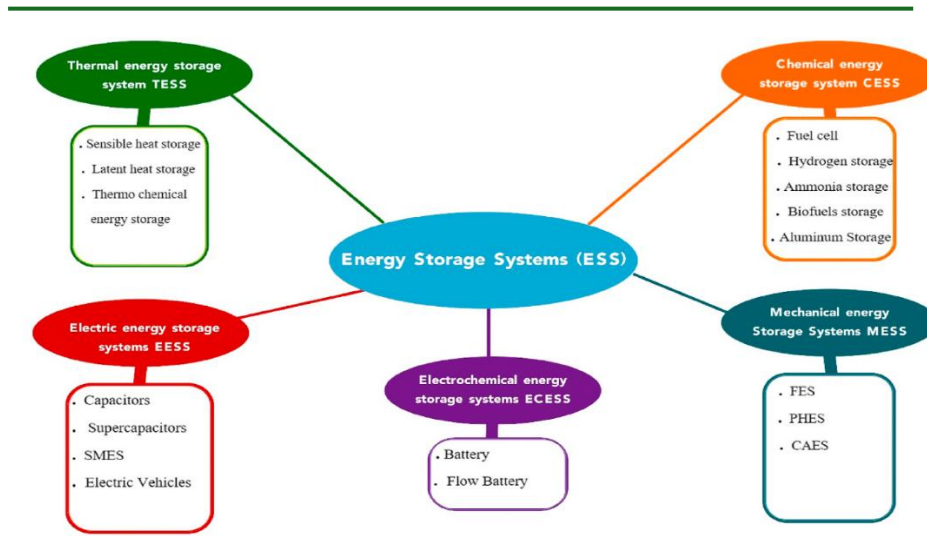


Figure 2 Classification of energy storage systems [20].

Among the cited energy sources, the employment of hydrogen as an energy carrier is still a promising route; it has many advantages like high long-term storage capability, hence, when the not immediately used renewable energy can be converted to hydrogen [21]. The hydrogen technologies still have many bottlenecks to obtain an efficient integration with clean energy sources [22]. Different ways can be used to convert the energy surplus into hydrogen [23], one of these methods is electrolysis, alkaline water electrolysis or proton exchange membrane (PEM) electrolysis; the results of this process are hydrogen and oxygen [24].

As just said, our society is strongly connected with electricity, and lithium-ion-based technologies are helping the decarbonization process, but this technology has several issues, like the employment of lithium, which is a critical raw material, according to the European Union, and it has a strong environmental impact [25]. The energy transition also requires new energy sources, cleaner than the old ones. Water splitting is a valuable route to satisfy this goal, for example, there

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is the possibility to employ solar energy to separate hydrogen and oxygen [26]. But in general, there are several challenges to obtaining more environmentally friendly water splitting systems [27].

Hence, new technologies are required to face climate change, continuing to work on decarbonization. For this reason, new classes of materials and devices are under evaluation, like transition metals, which can be employed as oxides [28] or dichalcogenides [29] for electrochemical energy storage applications. Nowadays, the revolution is not concerned only with the employed materials, but also the assembled devices need to evolve, indeed, common batteries are not efficient to decarbonize all automotive field, in this scenario, supercapacitors acquire great importance as a new solution [30].

1.2 Energy conversion: Alkaline water splitting

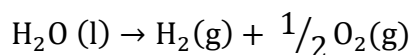
1.2.1 Water splitting overview

Green hydrogen represents a sustainable vector of energy towards green transition. Owing to its versatility and low environmental impact, it can substitute fossil fuels in industry, transportation, aviation and in several chemical and metallurgical industrial processes, thus mitigating the carbon footprint [31]. To date, the hydrogen demand is about 88 Mt per year, but it will increase to 2.3 Gt, for these reasons the term “hydrogen economy” acquired much interest recently [32].

Green hydrogen can be obtained through water electrolysis powered by electrical energy produced by renewable sources. The water splitting process involves two half-reactions, hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), occurring at the cathode and the anode of an electrolyzer cell, respectively. The best catalysts for HER and OER are Pt and Rh or Ir oxide, respectively [33], which are expensive, rare, and at high supply risk, therefore a pressing research goal is finding sustainable and efficient materials to replace them. The

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performance of the materials can be enhanced working on its features like the morphology, the number of active sites in the surface and the charge transfer resistance [34]. The bottleneck in water splitting is the OER kinetics which should be optimized; indeed, the overall reaction of water splitting is the following:



where $\Delta E^0 = +1.23 \text{ V vs RHE}$ and $\Delta G^0 = +237.2 \text{ kJ mol}^{-1}$. This is the general equation for water electrolysis as schematized in **Figure 3**.

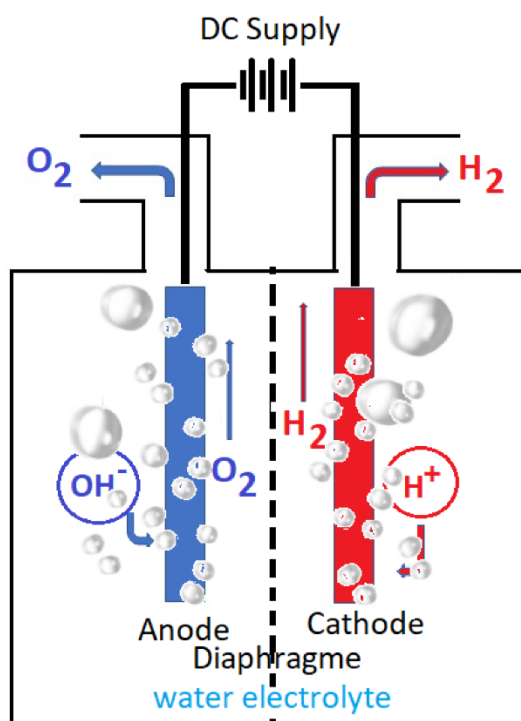
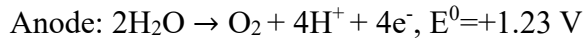
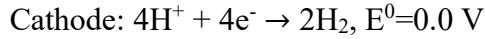


Figure 3 Schematization of a water-splitting cell [35].

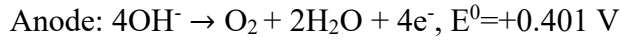
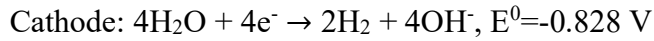
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The aqueous environment usually is enriched by electrolytes to increase the conductivity. These electrolytes can turn the water in alkaline using, for instance, KOH or NH_4OH , or acidic through the addition of H_2SO_4 . Varying the environment also the overall water splitting reaction have different products, as following[36]:

Acidic medium



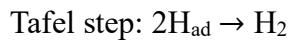
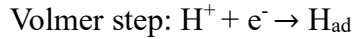
Alkaline medium



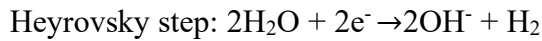
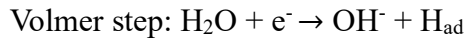
Hydrogen Evolution Reaction

As shown different reactions occur at the electrodes, like at the cathode in which a two-electron mechanism is observed, this reaction takes the name of Hydrogen Evolution Reaction (HER), because the output is the production of molecular hydrogen [37]. Different steps can be observed respect to the pH value during this reaction [38].

Acidic medium



Alkaline medium



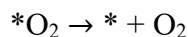
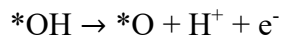
Tafel step: $2\text{H}_{\text{ad}} \rightarrow \text{H}_2$

Measuring the current, the rate-determining step can be extracted for each mechanism, in this way a study on the kinetics, hence the active mechanism, can be done. The goal is to obtain a smaller Tafel slope, between 30 and 40 mV dec^{-1} , respectively Tafel and Heyvrosky mechanism, while to the Volmer step is linked a slow kinetic with a Tafel slope around 120 mV dec^{-1} . Noble metal electrocatalysts are characterized by very fast kinetics, the challenge nowadays is to obtain similar values using non-noble metals.

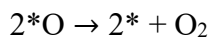
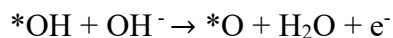
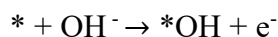
Oxygen Evolution Reaction

The second half of the water splitting reaction is the Oxygen Evolution Reaction (OER), it is a multistep reaction which occurs at the anode, involving four protons or electrons, in this case the result is molecular oxygen[39]. The kinetic for this reaction usually is slower than the HER due to the higher number of charges involved [40]. The reaction steps which occur for OER can be described using the following equations:

Acidic medium



Alkaline medium



considering * as catalysts active sites, and *O, *OH and *OOH are the adsorbed species [41]. The best materials for OER application are Iridium (Ir) and Ruthenium (Ru), electrocatalysts based on these materials are widely used but both are expensive and rare materials, indeed in the last decades the goal is to optimize electrodes avoiding their employment [42].

1.2.2 Alkaline Water Splitting

Focusing our attention on alkaline water electrolysis (AWE), there are several moments which mark the evolution of this technology (see **Figure 4**). Considering the used materials, the proper choice of electrode materials for the catalysts is critical to obtain efficient and cost-effective hydrogen. An AWE cell needs two electrodes, an anode and a cathode, which are separated by a membrane. Anode and cathode are characterised by the reactions which occur on them, oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) respectively. The OER is still the more critical of the two reactions. At the beginning, Platinum-based electrodes show promising performances [43], with a great capability to adsorb and activate different species on the surface [44]. To reduce the employment of a huge amount of platinum, scientists also evaluated the possibility of modifying its dimensions, also increasing the active surface area [45], [46]. Another step was taken, starting to study transition metal oxides (TMOs), which are abundant and cheaper than platinum [47]. Their great features increase the curiosity about this class of materials, combined with the possibility to produce TMO nanostructures [48]. Then, the nanoscale development of mixed-metal oxides improved the electrochemical performances of the electrodes, favouring also superior long-term stability. The Ni was one of the most considered elements for this purpose [49]. Recently, bifunctional materials have been gaining much interest; transition metal-based compounds can be employed for

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that. One of the most interesting is the nickel-molybdenum (NiMo) alloy [50].

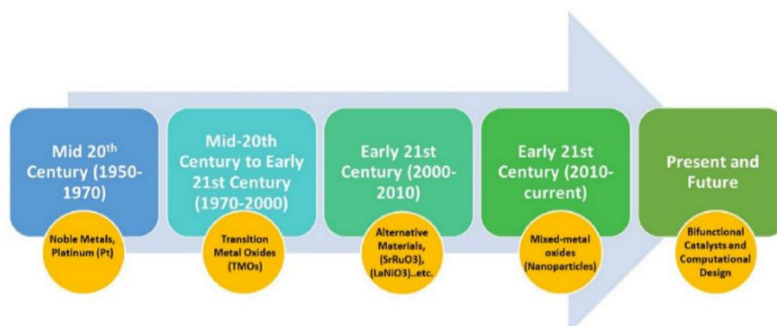


Figure 4 Development of materials for alkaline water electrolysis devices [44].

1.3 Energy storage: challenges and perspectives

The development of our society involves also the research of sustainable energy storage solutions with superior performances; for instance, new energy technologies are required for automotive field, mobile electronics and many other applications[51][52]. Then, the high environmental impact of classic Li-ion batteries is one of the reasons which justify the study of new path for the development of Electrochemical Energy Storage (EES) devices [53][54].

Nowadays, new electrochemical energy storage (EES) devices are studied to go beyond old ones, like devices based on Lithium [55]. EES can be divided in different classes respect to their performance, among these supercapacitors attracted much interest in recent years, thanks to their characteristics such as superior power density respect to Lithium-ion batteries [13], long stability up to 10000 cycles [56] and others [57]. For many years, metallic cations (sodium, lithium, calcium and zinc) were used for supercapacitor applications, but they have several issues, like high cost and environmental impact [54]. Hence many researchers proposed new routes, like the employment of non-metallic carriers, like

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ammonium or hydronium ions [58]; many of which are nontoxic, available at low cost and not aggressive for the electrode materials [59]. Ammonium ion-based supercapacitors attracted much interest thanks to their high energy density, about 10^2 Wh kg^{-1} , which is two orders of magnitude respect to classic supercapacitors [30]. Moreover, they allow storage at room temperature with high performances [60], [61]. The storage mechanism is studied in many works, it seems that ammonium ions form non-ionic chemical bonds with electrode materials, also known as H-bonds, but the mechanism kinetic is very sensitive to the morphology and material composition [62]. The further understanding of energy storage mechanism and to distinguish between intercalation, adsorption, and insertion mechanisms is still challenging for the development of supercapacitor devices [63]. There are many other open points related to this topic, as the employment of binder, indeed one of the future goals is the synthesis of binder-free electrodes [30]; and according to many works, morphology can be a path to enhance electrochemical energy storage [61], [64].

Recently, different classes of materials are evaluated to develop more sustainable devices [65]. High-Entropy Compounds (HECs), which belong to the class of High-Entropy materials, they are composed by 5 elements with the same ratio and rock-salts phase [66]. They show superior electrochemical performances respect to other members of the high-entropy materials family [67]. Another significant trend is the employment of carbon materials of natural origin, with the aim to improve both sustainability and suitability of the materials and processes [68]. For instance, in many works, lignin is employed to reduce the cost of these materials for supercapacitors applications [69]. Lignin is also employed for battery devices, to improve their sustainability [70]. New strategies for doping, synthesis and recovering of biomass are opening a new route of next-generation energy storage devices based on activated carbons [71].

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Between the different opportunities to develop energy storage materials the employment of transition metal is widely studied, indeed they offer great performances and stability [72]. Many works are concerned with two-dimensional transition metals, thanks to their features like high flexibility, ultrathin thickness, number of active sites on the surface, good conductivity and many others [73][74]. The features of these materials can be controlled using different techniques like morphology, doping, defects and hybridization [75]. Transition metals can be found in different compounds, such as Transition Metal Oxides (TMOs), which are a promising class of materials; indeed, their stability and the presence of many oxidation states are favourable for this application [28]. Their characteristics allow also the employment in cutting-edge applications like flexible supercapacitors, as studied by Delbari et al. [76]. Today not all TMOs are favourable to work, indeed for each material cost and social impact of their production are considered, hence the European commission published the Critical Raw Materials (CRMs) [33]. Among transition metals there is Molybdenum (Mo), which is a favourable material because it is not a CRMs and thanks to its interesting performances in energy storage applications [77][78]. Another possibility for the transition metals are the transition metal sulphides (TMSs); which represent another opportunity to employ of transition metal for energy storage applications, again their features guarantee great durability and stability [29]. Among TMSs, molybdenum disulfide (MoS_2) is one of the most widely studied in the literature [79]. Many works are concerned with the synthesis of 2D nanostructures based on MoS_2 [80]; 2D morphology seems to enhance its electrochemical activity. Usually, 2D- MoS_2 is combined with other materials to obtain heterojunctions which enhance the electrochemical energy storage performances, polymers and carbon-based materials are often used for this purpose [81], [82]. MoS_2 -based electrodes were also studied in different electrolytes, showing different performances, hence

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knowledge improvement about the connection between morphology and electrolyte is one of the recent goals in the field [62]. All the cited works use different binders in their mixture, it has important issues like the high environmental impact and the excess covering of the active surface, for these reasons, as just said, one of the goals for the future is the absence of binders in the material [30].

Hence, there are several classes of materials employed to develop new EES devices with a low environmental impact. But an important clarification is needed, indeed different materials can have different performances, or the same material in different electrolyte environments can change their behaviour. For what said, devices can be divided into different sections considering their electrochemical performances, a possible classification is done employing the Ragone plot, as shown in **Figure 5** [83], where different areas are highlighted considering specific power and energy.

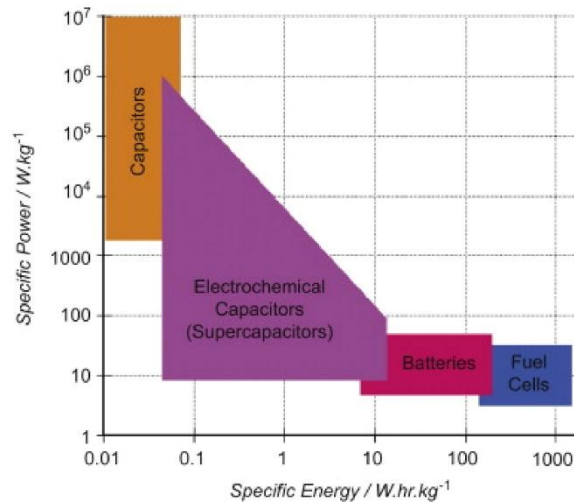


Figure 5 Ragone plot for different energy storage devices [83].

A comprehensive knowledge of the relation between materials and electrolytes in EES devices is a crucial point in this field [30]. Hence

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superior comprehension about storage mechanisms can open new routes to improve device electrochemical performances [84]. The materials can be distinguished also through the different mechanisms which occur during the electrochemical measurements [68].

An important category of materials is labelled as supercapacitors (SC), due to their superior performances as energy storage devices. These materials are characterised by the formation of an electrical double-layer as classical capacitor, but they also report high energy densities values [85]. The cited double-layer means that charge of opposite sign respect to the electrode are stored closely to the interface [85], indeed this mechanism is physical; it is characterized by fast and reversible processes, no chemical reactions are observed, suggesting a very long-life cycle [86]. For instance, carbon-based materials are widely studied for this purpose, thanks to their high surface area, but also due to the cost-effectiveness and their electrochemical stability [87]. But, 2D-TMDs can be a good alternative to carbon-based materials, indeed the morphology guarantee a superior surface area [80].

Many theories succeed to describe what happens at the interface, Helmotz firstly talked about the existence of a rigid layer close to the interface formed by ions with an opposite charge respect to the interface; this disposition forms the capacity behaviour (see **Figure 6a**) [88]. Then, Gouy and Chapman parallelly tried to overcome Helmotz theory with a model labelled as Gouy-Chapman model, they considered the ions layer as a diffuse one, hence it is not rigid (see **Figure 6b**), but this description fails for the high charged cases [89], [90]. The Stern model is a synthesis of the previous ones; indeed it describes the formation of a condensed layer at the interface when an electrical potential is applied, this takes the name of Stern layer, and it is divided into two sections, respectively inner Helmotz layer and outer Helmotz layer, the presence of adsorbed ions is recorded [91]. Beyond the Stern

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layer there is a diffuse one, its amplitude is a function of the applied electrical potential (see **Figure 6c**) [92]. In **Figure 6d**, there is a schematization of a EDLC with two high-surface electrodes (see **Figure 6e**). There are no chemical reactions when electrical double-layer is the dominant energy storage mechanism, for this reason the cyclic voltammogram profile has a quasi-rectangular shape, as reported in **Figure 6f**.

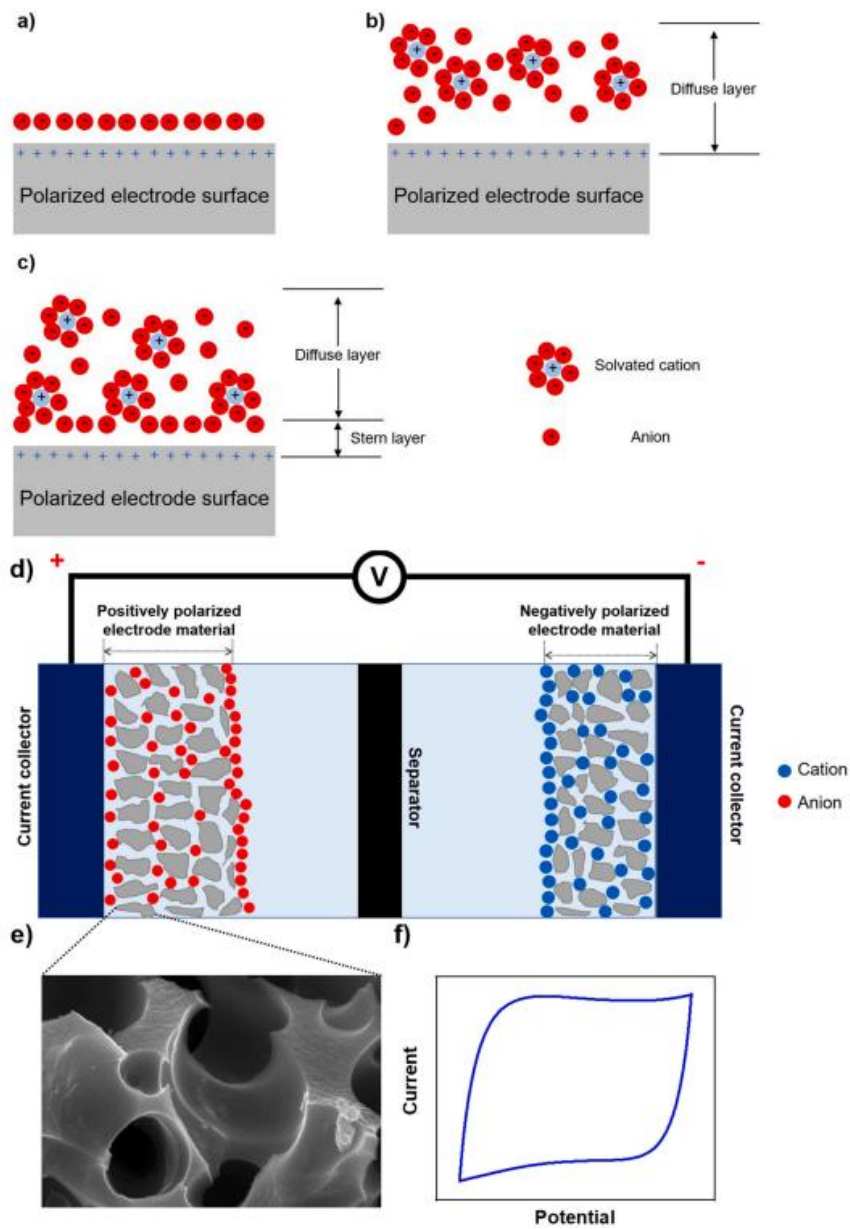


Figure 6 Models of an ECDL structure: a) Helmholtz layer; b) Gouy-Chapman layer; c) Stern layer. d) Schematization of an ECDL device with a e) porous electrode surface and its f) Cyclic Voltammogram profile [68].

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EDLCs are based on non-faradic reactions, hence without electron transfers, there is another class of materials which involves both faradic and non-faradic processes, they are labelled as pseudocapacitors [86]. **Figure 7a** shows the CV profile of a pseudocapacitor with non-faradic reaction, it has a quasi-rectangular shape close to EDLC one, while **Figure 7b** is linked to faradic process, reactions and peaks which occur at well-defined potentials and only at the surface, with a high-rate capability [93]. In **Figure 7c**, there is a schematization of a pseudocapacitor cell. Among faradic processes there are redox reactions, in this case oxidation and reduction reactions occur at the electrode-electrolyte interface varying the electric potential (see **Figure 7d**) [94]. **Figure 7d** shows the underpotential deposition at the interface, in this case the ions present in the electrolyte interact with the electrode interface due to the application of a potential, in this way there is a charge transfer and the formation of a monolayer at the interface [95]. There is a last faradic process which can happen at the interface, it is the ion-intercalation between the layers of the electrode material, again with electron exchange, but without variation for the crystallographic phase [96].

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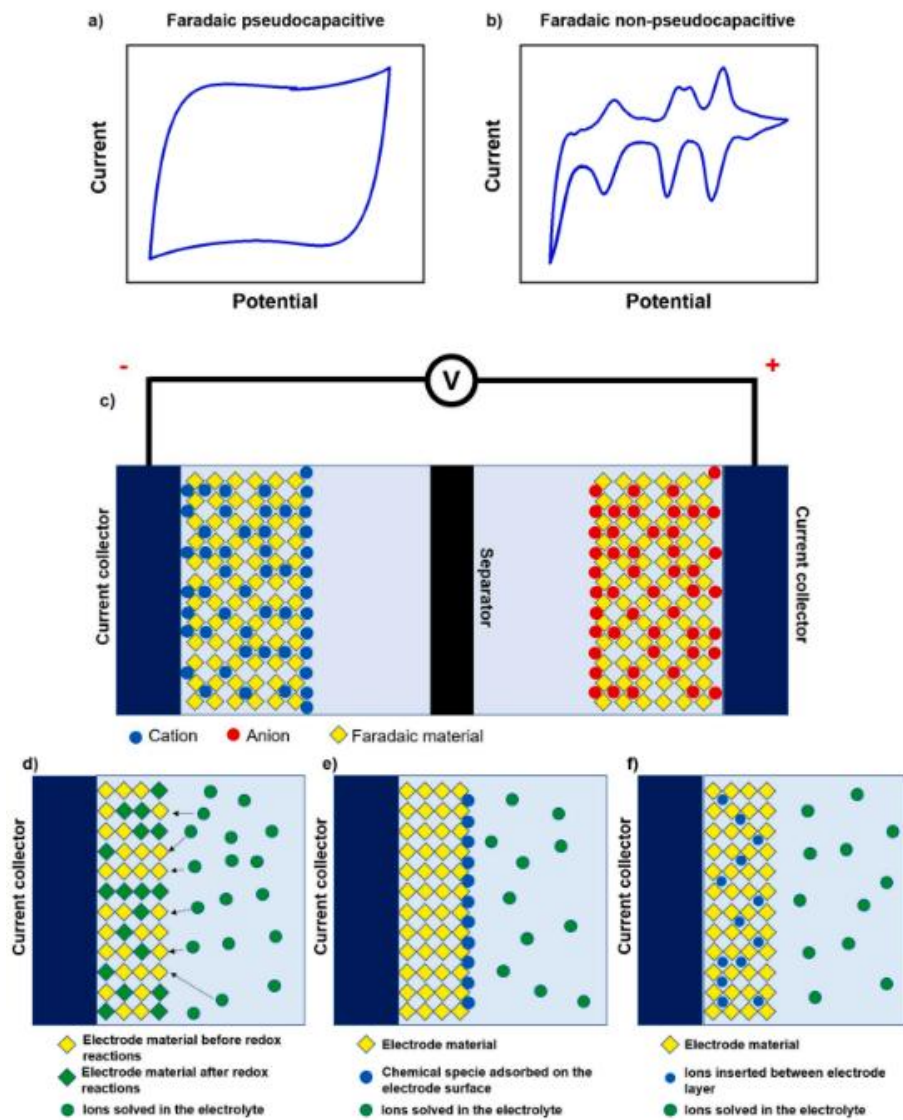


Figure 7 Cyclic voltammograms profiles for a) pseudocapacitive and b) non-pseudocapacitive energy storage devices; c) a schematized pseudocapacitor. Pseudocapacitance mechanisms: d) redox reaction, e) under-potential deposition, f) ion-intercalation [68].

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Another class of devices is labelled as hybrid supercapacitors (HSCs), here there is a combination of electric double-layer and battery-like mechanism [97], a possible schematization is shown in **Figure 8a**. HSCs take the typical power density of EDLC and the superior energy density of batteries devices, these devices are characterised by a wide operating potential window [98]. Different storage processes are involved, for example by non-faradic ones, and the galvanostatic charge-discharge profile has a triangular shape, like in **Figure 8b** [99]. There is also the possibility to have pseudocapacitance or battery-like storage, depending on potential, with a shape close to **Figure 8c**, but also a combination of all the processes, resulting in **Figure 8d**, which is a mixture of both behaviours [100].

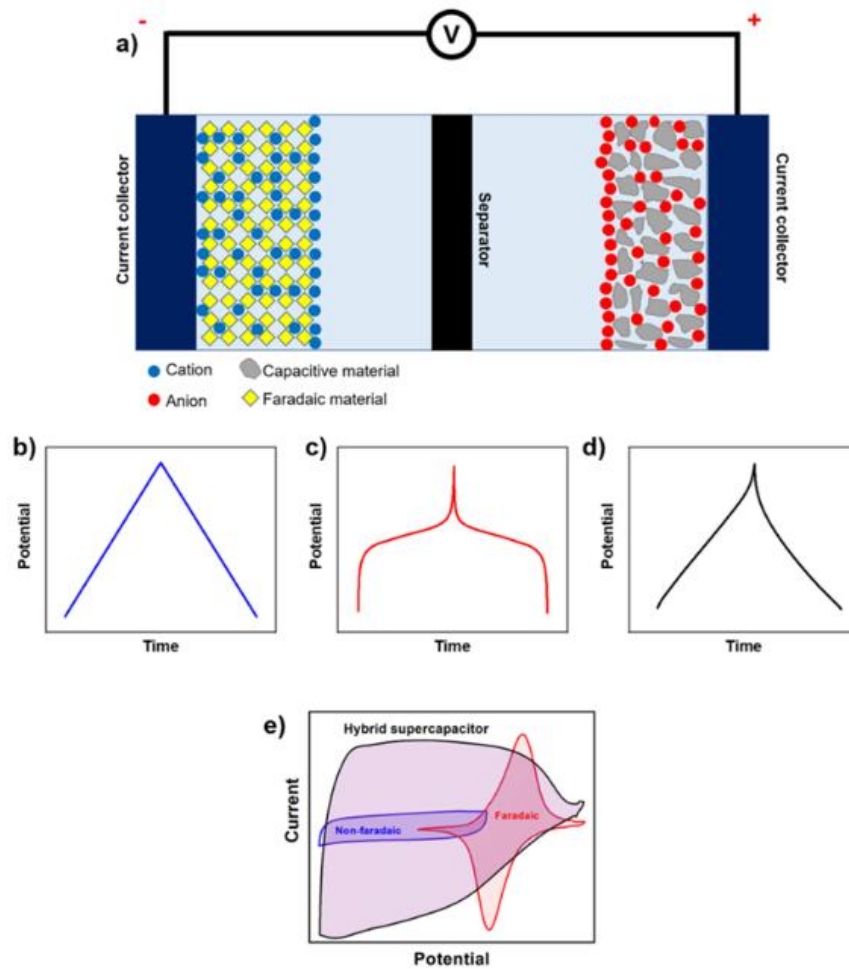


Figure 8 a) Schematization of a hybrid supercapacitor. Galvanostatic Charge and Discharge profiles of b) non-faradic; c) battery-like behaviour; d) combination of non-faradic and battery-like mechanisms. E) CV profiles of faradic (red) and non-faradic (blue) electrodes in a hybrid supercapacitor (black) [68].

1.3.1 Ammonium Ion Hybrid Supercapitors

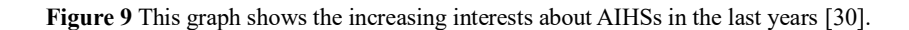
Hybrid systems are more suitable for consumer applications; for this reason, electrochemical energy storage systems which works as high-power supercapacitors and high-rechargeable batteries attracted much interests in the last years (see **Figure 9**), these devices are labelled as hybrid supercapacitors (HSCs) [101], [102]. Usually, metallic cations are employed in HSCs, like lithium, zinc and potassium, there are several issues connected to them, like high cost and difficulties in obtaining these resources [59], [103]. The possibility of producing high-performance HSC devices employing ammonium ions was recently reported by Chen and colleagues [104]. Then, many other works started to study that, indeed, ammonium-ion hybrid supercapacitors (AIHSs) show high power and energy density, with better long-term stability than other metallic carriers [63]. The NH_4^+ ion can be found in a mildly acidic or neutral aqueous electrolyte, allowing less corrosion of the electrode [105]. Between ions and the electrode, nonmetallic H-bonds are formed, which improves the reversibility of the mechanism, enhancing the electrochemical performances [106]. The AIHS device is composed of two electrodes, one of which works as an electric double-layer capacitor for the anode, while the other acts like a pseudocapacitor for the cathode [63], [104]. Also, in this case, the nanostructuring of the materials increases the number of active sites, enhancing the electrochemical performances [107].

One of the main differences between AIHSs and other HSCs based on spherical metal ions is that NH_4^+ has a preferential direction due to its tetrahedral structure, which influences the storage mechanism and the interaction with the host sites [108]. Different processes are observed for the storage of the charge. Firstly, there is the possibility to observe intercalation/deintercalation of NH_4^+ ions, which is a reversible process, in which ions interact with the crystal lattice, without significant degradation of the material [109]. Another important

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mechanism that we can observe is the coinsertion/extraction of NH_4^+/H^+ ions, it involves the presence of H vacancies exposing more electronegative sites which act as active ones, favouring cation adsorption on the surface. The exposed mechanism is sensible to the electrolyte concentration; indeed a low concentration means a higher number of free water molecules which takes part to the coinsertion [110]. A part of the stored charge is also linked to the adsorption/desorption of NH_4^+ ion [111] and conversion reaction, which implies a charge transfer [112].

Despite the huge amount of works about AIHSs, there are still several open points, like a deeper understanding of active mechanisms during the measurements, which requires the adoption of different in operando techniques. Suitable designs are under evaluation to enhance the electrochemical performances. Electrolytes' optimization is also a crucial point to improve these devices; this is strongly connected to the possibility of having binder-free electrodes [30].



A key role in fighting climate change is taken by nanostructures, thanks to their wide range of applications in different fields, from agriculture to water purification and energy storage and conversion. All that thanks to their surface-volume ratio favourable to conjugate high performance and a low employment of material with respect to applications with bulk materials [80][113]. Thanks to their unique shape and size, different effects can be seen, like quantum confinement effects and highly altered surface energy, modifying the bond structures close to the material's surface[114][115].

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The nanomaterials can also offer superior performance with respect to classic ones for different applications, as shown in **Figure 10**, helping to reach sustainable goals [116]. There are multiple fields of application for the nanomaterials; they can be employed for greenhouse capture and the production of biofuel [117]. The nanomaterials can also be used for biofiltration in membranes; indeed, they can separate ethanol from other compounds [118]. Similarly, nanocapillary graphene materials are employed for membranes in water purification [119].

Nanomaterials can also be employed as highly efficient electrocatalysts for water splitting reactions; they can achieve good strength to the substrate, high activity, selectivity for the reactions and very fast kinetics [36]. For instance, 3D nanomaterials with hierarchical structures are gaining much interest among scientists, as they offer enormous surface area and electroactive sites at the interface with the electrolyte [120]. Different morphologies are tested, from nanoflowers [121] to an array of nanodomes [122].

For energy storage applications, the nanostructures offer different features, like in high-rate batteries, because nanomaterials are less subject to phase transformation during insertion and de-insertion respect to larger particles [123]. Li-ion batteries are widely used due to the rapid increase in the demand for electric vehicles, but there are several issues related to these technologies [55]. New opportunities are valued to avoid the employment of lithium, and nanostructures can play a key role in this game; indeed, sodium and potassium-based batteries are considered promising routes for the future [124].

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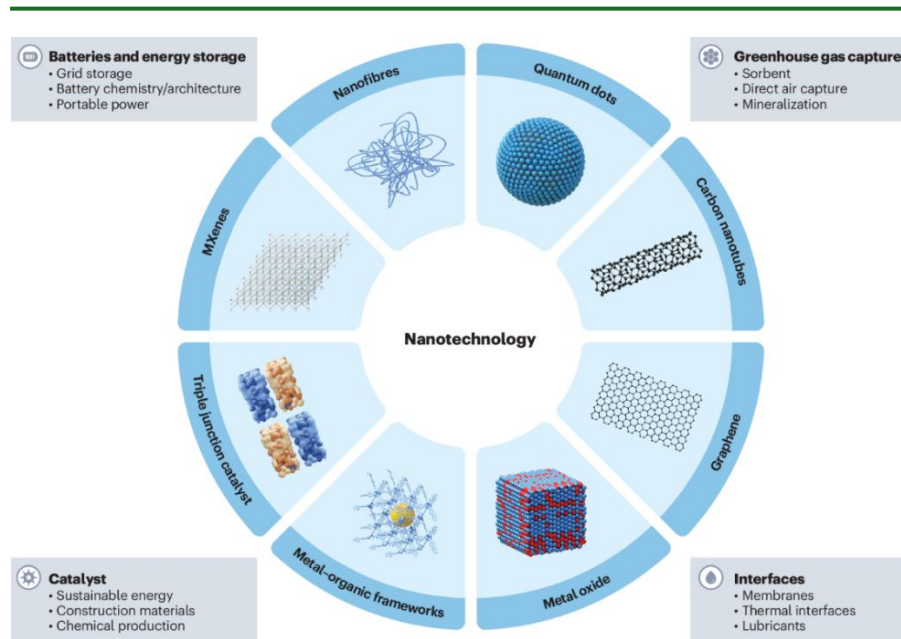


Figure 10 Examples about how nanostructures can be a solution for different fields [125].

1.5 Urban mining and circular economy

The shift to a circular economy was much discussed in the last years [126], for this reason many researchers are studying solutions to recover materials from waste, as Kim et al. in their work in which they put their attention on recovering materials in hydrometallurgical processes [127]; or Aloraini and Saees which focused on recycling Pb from exhausted lead-acid batteries to produce polymeric-based materials [128]. The recycled material can be the starting point for the development of new technologies [129] as shown in **Figure 11**. This consideration of waste as a resource is labelled as “urban mining”, and it is a good practice well-accepted by many scientists today, especially regarding e-waste materials [130]. In this context, the possibility of

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developing materials easy to recycle is important, as shown by Lin et al. [131].

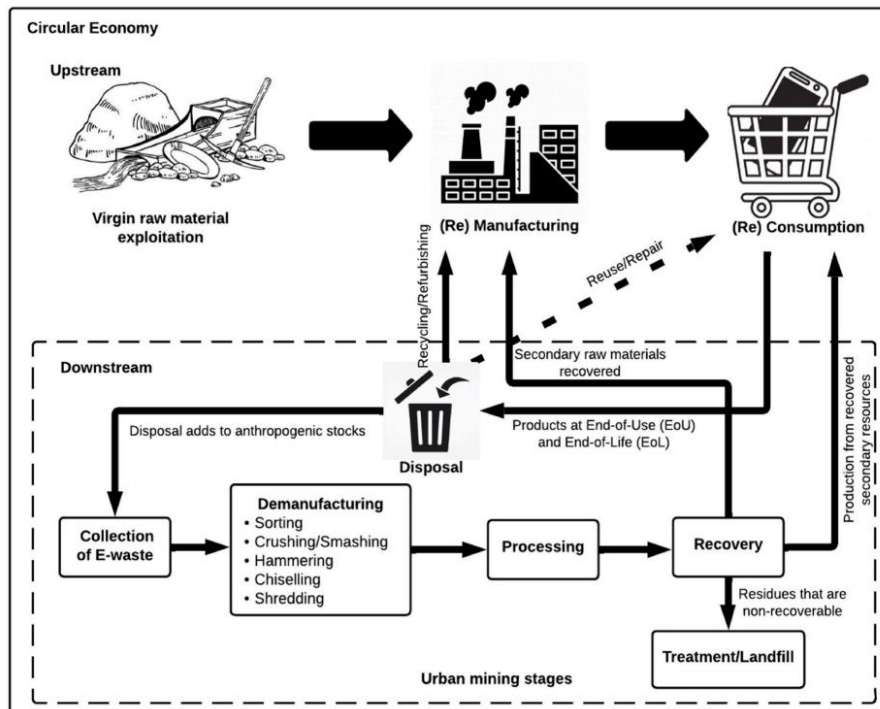


Figure 11 Schematization of circular economy and e-waste urban mining process [132].

The management of waste is another crucial point for the development of our society [133], hence many tests were done to recover materials from waste produced during the development of many devices, like batteries [33]. It was proven that urban mining policies can reduce energy consumption, as described by Shen et al. in their study of some areas of China [134].

Many examples of applications for recycled materials can be found in the literature [48]. In this view, the synthesis of Mo oxide and sulphides starting from industrial waste can be of large interest as sustainable electrocatalysts for hydrogen production. Moreover, the increasing use

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of Mo in the steel industry, oil and gas industry, corrosion-resistant alloys, cast iron, and catalyst industries makes it increasingly required and expensive [135].

1.6 Aim of the work

The reported research wants to be a bridge between circular economy and electrochemistry. Indeed, this work is concerned with the conversion of recycled molybdenum-based powder to valuable nanostructures for energy conversion and storage.

Chapter 2 starts with a characterization of the molybdenum-based recycled powder. Then, three different syntheses of nanostructures were shown, all of them employing the hydrothermal treatment, which is considered a cost-effective method, also easy to scale-up to industrial levels. Firstly, MoO_3 -nanobelts were obtained, which were sulfurized to obtain $\text{MoS}_2/\text{MoO}_3$ -nanostructures; finally, MoS_2 -nanosheets were directly obtained from recycled material.

In Chapter 3, the nanostructures previously synthesised were characterized for oxygen evolution reaction and hydrogen evolution reaction. Finally, they were employed to build an overall water splitting cell in alkaline electrolyte.

MoO_3 -nanobelts and MoS_2 -nanosheets were both studied for energy storage application in Chapter 4. A comprehensive study of the active energy storage mechanisms for MoO_3 -nanobelts in different alkaline electrolytes was performed. MoS_2 -nanosheets were studied in ammonium sulphate, again the active mechanisms were analysed.

A step beyond to the classical characterisation is reported in Chapter 5, here MoS_2 -nanosheets were employed to assemble a proof-of-concept device, but firstly a study on the effect of the substrate on the electrochemical performance is shown.

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Chapter 6 collects all the conclusions from the previous chapters, highlighting both reached goals and multidisciplinary results obtained. Showing the importance of this work as bridge between different fields, opening new routes for more environmentally friendly devices.

From industrial waste to Mo-based nanostructures

Chapter 2. From industrial waste to Mo-based nanostructures

2.1 Characterization of the Mo-based recycled powder

The Mo-based powder precursor, provided by Spirit S.R.L. (Chiampo, Vicenza, Italy), was obtained after thermal treatments (in a muffle, 700 °C for 3h) of metal industrial waste and it was commercially denominated as recycled P-MOXX. This precursor, labelled as R0, has not a defined nanostructured morphology. Low and high-magnification Scanning Electron Microscopy (SEM, Appendix A) images of R0 are reported in **Figure 12a** and **Figure 12b** respectively. **Figure 12a** shows spheres with a diameter of 4-5 μm ; while, going to higher magnification (see **Figure 12b**) no well-defined nanostructures are reported. Hence, it is possible to conclude that the recycled material has not a defined nanostructure shape.

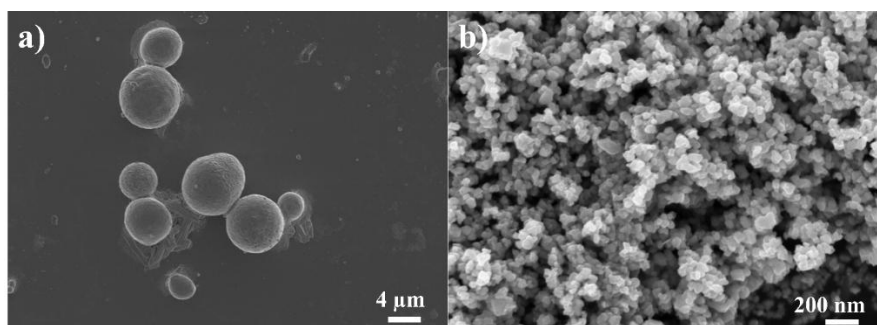


Figure 12 The SEM images of the Mo-based recycled powder are reported with a) low- and b) high-magnification.

X-Ray Diffraction (XRD, Appendix A) pattern of R0 is reported in **Figure 13**, it shows that the material is mostly composed of a mixture

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of metallic molybdenum (peaks at 40.56° and 58.76° , labelled with M, Card No.: 00-089-5023) and molybdenum dioxide (peaks at 26.06° , 36.88° and 53.60° , labelled with asterisk, Card No.: 00-076-1807).

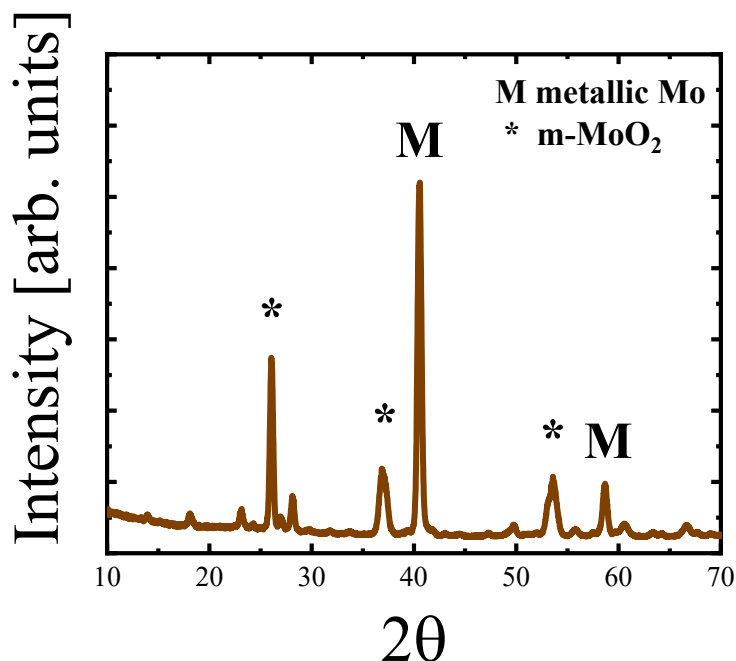


Figure 13 The XRD pattern of the Mo-based recycled material, here were added markers for m-MoO₂ and metallic Mo.

The Rutherford Backscattering Spectroscopy (RBS) was also employed to further study the presence of different oxidation states of molybdenum (see Appendix A for insights on the techniques). The RBS pattern confirms the XRD considerations (see **Figure 14**); indeed, a ratio between the doses of O and Mo of about 2 was found, confirming the presence of molybdenum dioxide (MoO₂) in the sample.

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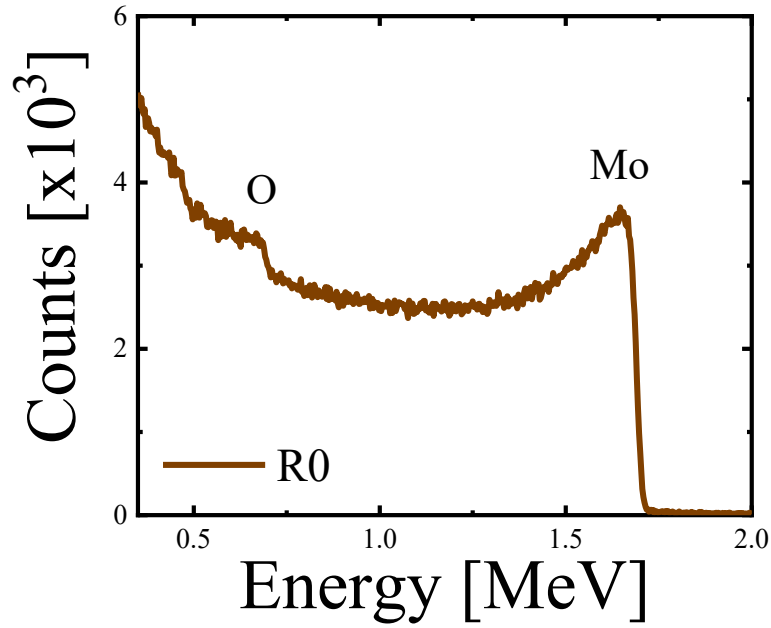


Figure 14 The RBS pattern of the Mo-based recycled is reported here, markers for oxygen and molybdenum were added.

The optical bandgap of the material was estimated by dispersing them in deionized water and measuring the transmitted light intensity. The product αt was calculated using the Beer-Lambert law [136], see Eq.1 (see Appendix A). **Figure 15** reports the Tauc plots of $(\alpha h\nu)^{1/n}$ as a function of photon energy, $h\nu$, with $n=1/2$ because we assume that the samples have direct bandgap transitions [137]. The extrapolated intercept with the x-axis gives an estimation of the optical bandgap. R0 reports an optical bandgap of 4.3 eV linked to pure MoO₂ [138].

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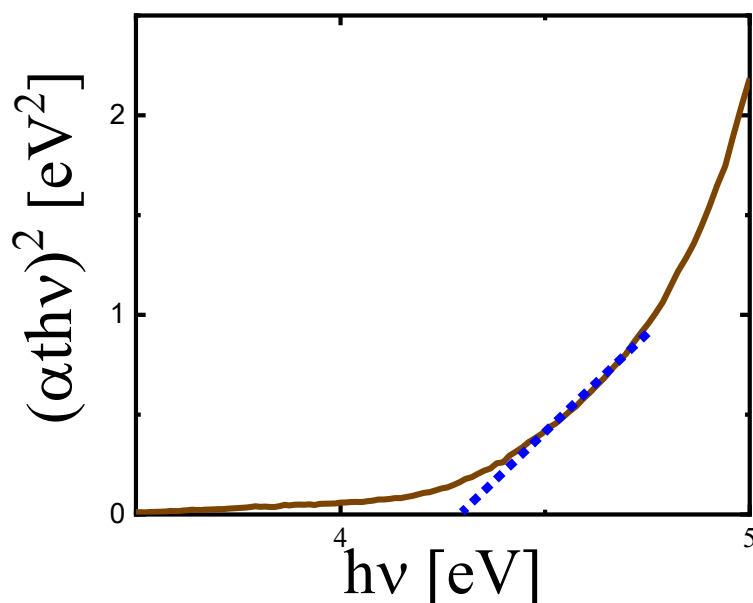


Figure 15 UV-Vis spectrum of R0, the straight line of the fit is reported in blue, highlighting the intercept with the x-axis.

The characterization performed on the recycled materials highlights a huge presence of m-MoO₂, with some components of metallic Mo, as seen by XRD pattern. This recycled material is the starting point for the syntheses reported in the following paragraphs, these will be employed for different electrochemical applications in the following chapters.

2.2 MoO₃-nanobelts

2.2.1 Synthesis procedure

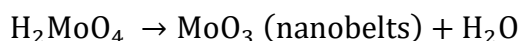
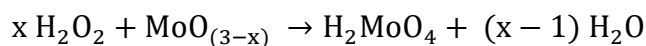
The first synthesis performed employing the recycled material was the one to obtain MoO₃-nanobelts, it consists in a two-step process (see **Figure 16a**), which was optimized to obtain nanobelts morphology. The process starts from Mo-based powder precursor (see **Figure 16b**). As

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just said, the starting material has not a defined nanostructured morphology, as also reported in **Figure 16c**; while one of the synthesis's goal is to obtain a well-defined shape for the material, with a nanosize.

Firstly, an exothermic reaction between recycled Mo-based powder (labelled as R0) and hydrogen peroxide (H_2O_2 , %30 wt, Sigma Aldrich) occurred, mixing 0.5 g of R0 powder with different amounts of H_2O_2 as reported in **Table 1**. The ratio of H_2O_2 mass to that of R0 powder gives the name to the sample, as described in **Table 1**, so that N18 describes a solution of 9 mL H_2O_2 with 0.5 g of R0 powder. The obtained peroxo-molybdic acid solution was characterized by a yellow colour (see **Figure 16d**), it was magnetically stirred for 30 minutes. Different amounts of hydrogen peroxide were used, controlling the pH for each of them, and studying its effect on the resulted material (**Table 1**). SEM images of the peroxo-molybdic solution were taken, as reported in **Figure 16e**.

During the first step of MoO_3 nanobelts synthesis, different exothermic reactions may occur leading to several peroxo-molybdate species [139], [140]. The peroxo-molybdate species are generally unstable and evolve into molybdic acid and then, into MoO_3 nanobelts. Thus, to describe the initial stage of the synthesis we can consider the resulting Equations [141], [142]:



The effect of hydrogen peroxide during the process was tested by varying the amount of H_2O_2 during the synthesis (**Table 1**). Each synthesis procedure is labelled thus taking into consideration the H_2O_2 added amount. The N0 sample was obtained without any H_2O_2 addition, by using R0 dispersed in deionized water as a precursor (no exothermic reactions occurred).

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Table 1 MoO₃ nanobelt synthesis summary. The mass of the starting Mo-based powder (R0) was fixed to 0.5 g.

Name	H_2O_2 [mL]	H_2O_2 : R0	pH
N18	9.0	18	1.26
N14	7.0	14	1.35
N7	3.5	7	1.60
N0	0	0	2.35

The second step was the hydrothermal treatment (HT): the obtained peroxy-molybdic acid solution was transferred into a Teflon liner and deionized water was added to obtain a volume of 25 mL. The liner, put into an autoclave, was inserted in a muffle (see **Figure 16f**) for 3 hours at 180 °C, after which the solution was left to cool to room temperature for 18 hours. The resulting solution was centrifuged (6000 rpm for 10 min), washed with ethanol and deionized water, and dried on a hot plate (75 °C for 45 minutes) to obtain the dried MoO₃nanobelts powder, as shown in **Figure 16g**.

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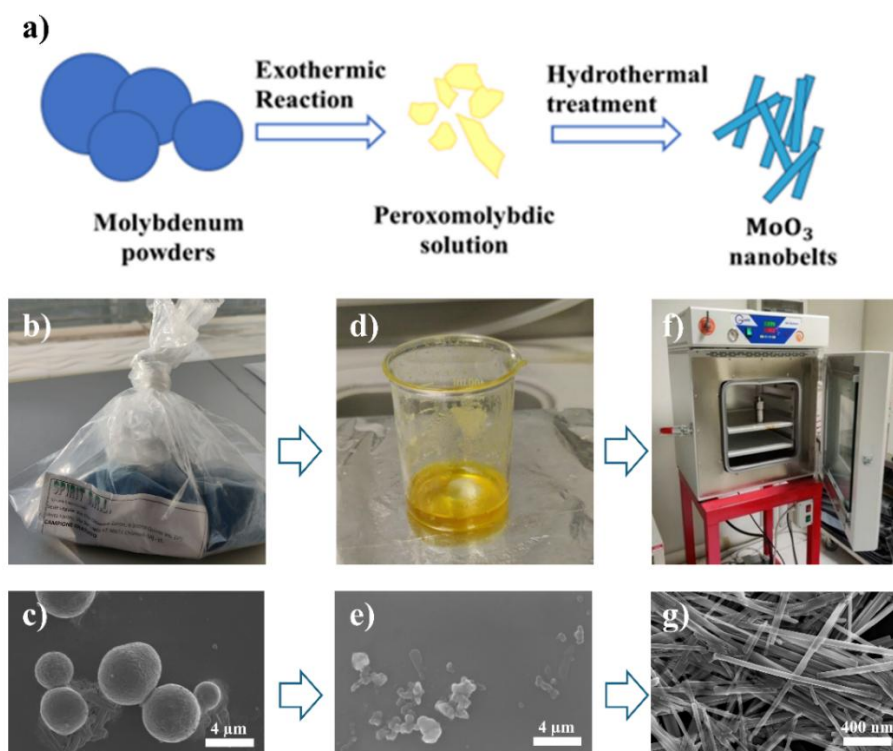


Figure 16 Scheme of the synthesis of MoO₃ nanobelts.

2.2.2 Morphological and Phase characterization

After the hydrothermal treatment, the solutions were dried and studied to evaluate both morphologies and phases. **Figure 17** reports the morphology of N0, N7, N14 and N18 samples respectively. At higher pH values there are still spheres and debris in the samples, but we can also see the presence of elongated structures. By increasing the H₂O₂ amount the presence of the spheres decreases with the pH, and at more acidic pH values only elongated (50-100 nm in section, several μm in length, called nanobelts), are present, thus suggesting a beneficial role

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for H^+ ions in the conversion of peroxy-molybdic acid into orthorhombic MoO_3 .

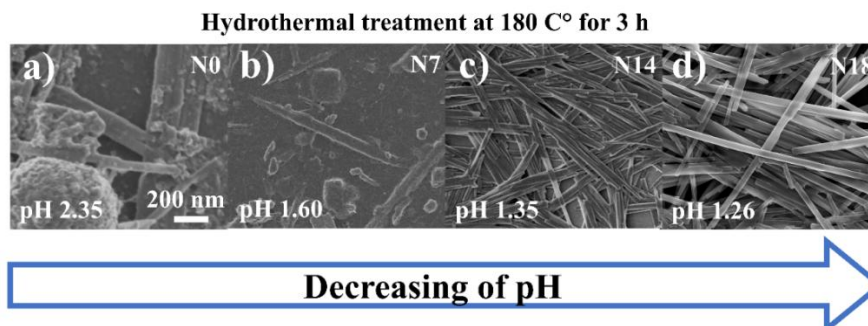


Figure 17 Powders obtained after the hydrothermal treatments conducted by using the pH 2.35 (N0), the pH 1.35 (N14), the pH 1.60 (N7) and the pH 2.35 N0 synthesis, respectively. The scale bar is 200 nm for panels

In **Figure 18a** the XRD patterns of two MoO_3 nanobelt samples (N7 and N18) are reported, together with that of the starting Mo-based powder (R0), for comparison. The N7 sample shows a clear MoO_3 crystal structure, even if two different phases are present: orthorhombic MoO_3 (12.76° , 25.74° and 39.04° 2θ peaks, labelled with a full circle, Card No.: 00-005-0508) and monoclinic MoO_3 (23.1° and 47.28° 2θ peaks, labelled with a full rhombus, Card No.: 00-047-1320). This confirms the possibility to have a coexistence of α - MoO_3 and m- MoO_3 , as expected [143]. N18 sample presents XRD peaks linked only to orthorhombic MoO_3 (12.76° , 23.42° , 25.76° , 27.3° , 39.02° and 58.9° 2θ peaks, labelled with a full circle). For the orthorhombic phase of N7 and N18 the most intense peaks are referred to (0k0) growth direction, that is the preferential nanobelts growth direction, which is a consequence of surface energy modification along the other directions [144]. Thus, suggesting that the high concentration of H^+ ions in solution, confirmed by the very low pH values recorded, helps to saturate the dangling bonds along (00h) and (m00) directions [144].

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Figure 18b shows the Raman spectra of four MoO₃ samples (N0, N7, N14 and N18). N0 sample shows rough peaks at 649, 722, 803 and 968 cm⁻¹, pointing to the presence of MoO₂ (labelled with asterisk), α-MoO₃ (labelled with a full circle) and m-MoO₃ (labelled with a full rhombus) [138]. N7, N14 and N18 samples show more evident peaks, at 663, 819 and 991 cm⁻¹, related to α-MoO₃ [145], which is the most stable phase of the molybdenum trioxide. It should be noted that N7 spectrum shows two further peaks at 778 and 904 cm⁻¹ [143], characteristic of m-MoO₃, thus confirming XRD analysis. These results suggest that for our synthesis a low pH value is beneficial for obtaining a pure α-MoO₃ crystal phase, probably due to the large abundance of H⁺ ions favouring the reaction of peroxo-molybdate species.

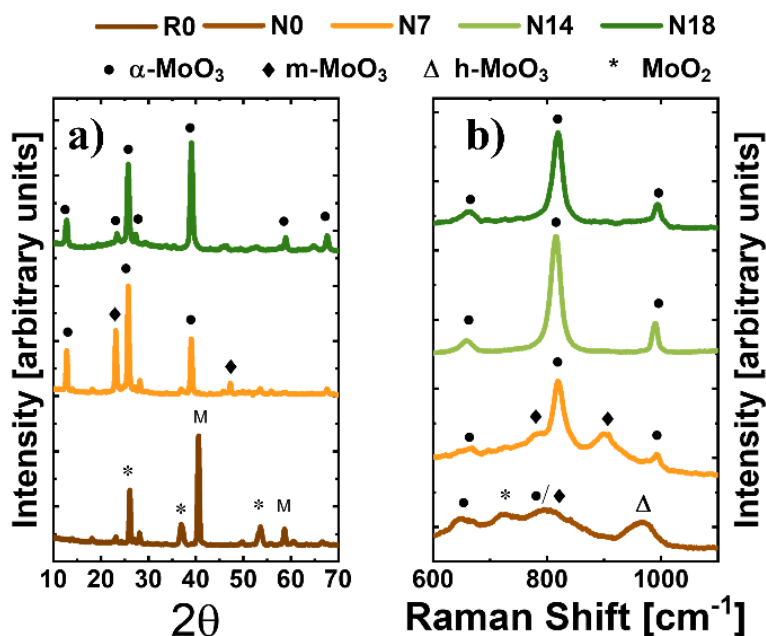


Figure 18 a) XRD spectra of Mo-based starting powder (brown curve), synthesis N7 (orange curve) and N18 (dark green curve). Symbols refer to different crystal phase reflections, while “M” stands for metallic Mo reflections. b) Raman spectra of nanobelts prepared at pH 2.35 (light brown curve), pH 1.60 (orange curve), pH 1.35 (light green curve), pH 1.26 (dark green curve).

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Figure 19 reports the Tauc plots, hence $(\alpha h\nu)^{1/n}$, where α was calculated using Eq.1 (see Appendix A), as a function of photon energy, $h\nu$, with $n=1/2$ because we assume that the samples have direct bandgap transitions [137]. The extrapolated intercept with the x-axis gives an estimation of the optical bandgap. For N7, N14 and N18 the optical bandgap is about 3.3 eV, which is in good agreement with that of bulk α - MoO_3 [146], [147], while for N0 it is equal to 3.5 eV, as expected considering that MoO_2 bandgap value reported in the literature is a bit higher than that of α - MoO_3 , which is quite lower than R0 as just seen it is linked to pure MoO_2 [138]. The optical bandgap values decrease with the pH, hence these estimations further confirm the effect of hydrogen peroxide on the stoichiometric composition of nanostructures through the different syntheses.

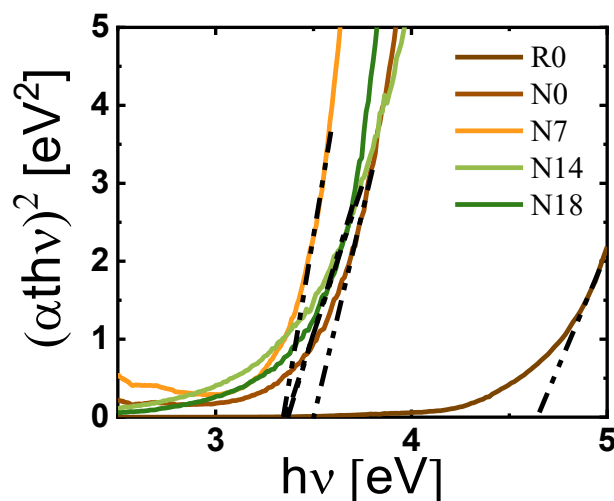


Figure 19 Tauc plot for the MoO_3 nanostructures syntheses and Mo- based starting powder.

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2.2.3 Conclusions

In this first part of the PhD project, MoO₃-nanobelts were synthesised from recycled industrial waste through a cost-effective two steps process. Controlling the pH value of the peroxo-molybdic solution, resulted by the exothermic reaction, I was able to modify both morphology and phase of the resulting material. As suggested in the past, H⁺ acts as a capping agent for the material growth [144], leaving the c-axis direction free. The resulted nanostructures were elongated, for this reason we labelled them as “nanobelts”. Seeing XRD patterns and Raman spectra, it is possible to observe the transition from the starting mixture of metallic Mo and m-MoO₂ to pure orthorhombic MoO₃ (α -MoO₃). Thanks to UV-Vis Spectroscopy we were also able to evaluate the optical bandgap of the different samples, finding a shift from the one linked to m-MoO₂, about 4.5 eV, to 3.3 eV which is typical for α -MoO₃.

2.3 Mixed Mo sulfide-oxide nanostructures

2.3.1 Synthesis procedure

MoO₃-nanobelts powder, obtained as described in the previous paragraph, was employed for the synthesis of MoS₂/MoO₃ nanostructures. Different syntheses were performed, employing a one-step hydrothermal synthesis (as schematized in **Figure 20**) with the goal to optimize the ratio between MoO₃-nanobelts powder and thiourea (TU, by Sigma-Aldrich), which acts as a sulphur precursor for the Mo-based nanostructures. The goal of this part was the synthesis of a blended material. A synthesis using the Mo-based recycled powder was also performed to highlight the effect of the nanostructurization of the starting material.

MoO₃-nanobelts powder (22 mg of N18 sample) was magnetically stirred for 30 minutes with different amounts of thiourea and 15 mL of

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deionized water. The tested ratios were reported in **Table 2**, here is also present the synthesis done using R0 material, which was labelled as SR5.0. The molar ratio of TU to MoO₃ powder gives the name to the sample, so that SN7 describes a solution of 80 mg TU with 22 g of MoO₃-nanobelts powder. Once stirred, the solution was transferred into the Teflon liner, inserted in an autoclave, and placed in a muffle for 3 h at 180 °C. The autoclave was then cooled at room temperature for 18 h, and the obtained product was centrifuged and washed with water and ethanol at 6000 rpm for 30 minutes. The resulting solution was concentrated at 100 °C under nitrogen flux for about 4 hours.

Table 2 MoS₂/MoO₃ nanostructures syntheses summary

Name	Molybdenum based powder [mg]	Thiourea (TU) [mg]	TU/ MoO ₃ [molar ratio]
SN2.5	22 (N18)	34	2.5
SN5.0	22 (N18)	57	5.0
SR5.0	22 (R0)	57	5.0
SN7.0	22 (N18)	80	7.0

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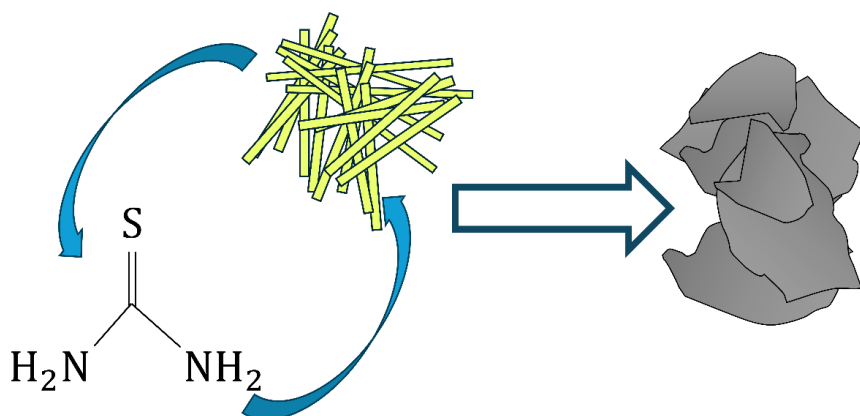


Figure 20 MoO₃ nanobelts were sulfurized to obtain a blended MoS₂/MoO₃ nanostructures.

2.3.2 Morphological and phase characterization

SEM analysis shown in **Figure 21a-d** demonstrates that by increasing TU, the size and shape of obtained nanostructures change. SN2.5 SEM image (see **Figure 21a**) could give a hint of the nanobelt fragmentation, and SEM image of SN5.0 (obtained by increasing TU/MoO₃) shows the presence of irregular debris (see **Figure 21b**), with a side of about 300 nm. **Figure 21c** reports the SR5.0 sample, in which, despite the use of the same molar ratio of SN5.0, very thin irregular structures are present. This points out the importance of using a MoO₃ nanobelts powder in place of the R0 powder. At well higher TU/MoO₃ ratio (SN7.0) irregular structures aggregate in a jagged network (see **Figure 21d**). The addition of TU activates the sulfurization of Mo oxide powder, leading to a fragmentation of original nanobelts. A smaller amount of TU probably affects only the surface of the starting powder, leaving traces of the nanobelts, while a too-large amount of TU destroys every memory of the nanobelts. It seems that a medium TU amount can give the best results as the MoS₂ formation is concerned.

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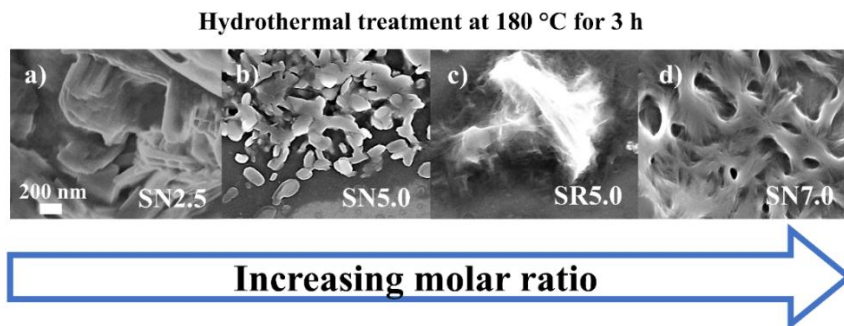


Figure 21 SEM image of samples with different TU/ MoO₃ molar ratio: SN2.5 (c), SN5.0 (d), SR5.0 (e) and SN7.0 (f), the same scale bar was used for all the syntheses.

Figure 22a shows the XRD spectra of different samples. As well known, the nanometric size of our materials affects the peaks, producing shifts and broadening [148]. SN2.5, SN5.0, SN7.0 and SR5.0 samples show a peak at 14° (green vertical band) which can be linked to (002) plane of 2H-MoS₂. Only SN5.0 sample reports also the other expected peaks at 40° and 57° (green vertical bands), related to (103) and (110) planes of 2H-MoS₂, respectively [80], [148], [149], [150], [151]. Other peaks were recorded, like those around 12° and 52°, which are assigned to α -MoO₃ (Card No.: 00-005-0508). The presence of MoO₂ can be suggested by the peaks at 19°, 37° and 57° (Card No.: 00-076-1807). According to XRD patterns, the treatment in HT with TU modifies the α -MoO₃ nanobelts by reducing it and adding MoS₂ phases, as expected.

Figure 22b reports the Raman spectra of the samples, which show Mo-S bond peaks, at around 370 and 405 cm⁻¹ (E_{2g}¹ in-plane and A_{1g} out-plane phonon modes, respectively, highlighted in the green region) [152]. SN2.5 sample does not present defined peaks, this suggests that only a few numbers of Mo-S bonds were formed; while increasing the TU ratio it is possible to see E_{2g}¹ and A_{1g} peaks, with $\Delta\kappa$ equal to 38 and 30 cm⁻¹, respectively for SN5.0 and SN7.0. The $\Delta\kappa$ difference

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between these two peaks is an important datum, since in MoS_2 materials the interlayer distance among MoS_2 planes increases when $\Delta\kappa$ decreases [153]. According to the literature, the low difference between these two peaks can be related to a few-layered structure, as recorded in the last two samples [153]. SN2.5 and SN5.0 samples still report broadened peaks between 270 and 330 cm^{-1} , which can be attributed to the presence of large amounts of molybdenum oxide [145]. SN2.5 has a defined peak around 950 cm^{-1} assigned to $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ [154], also SN7.0 reports this peak together with one at 760 cm^{-1} which can be a convolution between MoO_2 (743 cm^{-1} [138]) and $\text{MoO}_3 \cdot \text{H}_2\text{O}$ (776 cm^{-1} [154]), while SN5.0 is characterized by monoclinic (786 and 903 cm^{-1} [143]) and orthorhombic (660 and 820 cm^{-1} [145]) peaks. The different widths of the peaks can be attributed to the effect of the boundaries, according to the presence of nanostructured material [155]. Raman spectra highlight the presence of Mo-S and Mo-O bonds compatible with MoS_2 , MoO_3 and MoO_2 , confirming XRD conclusions.

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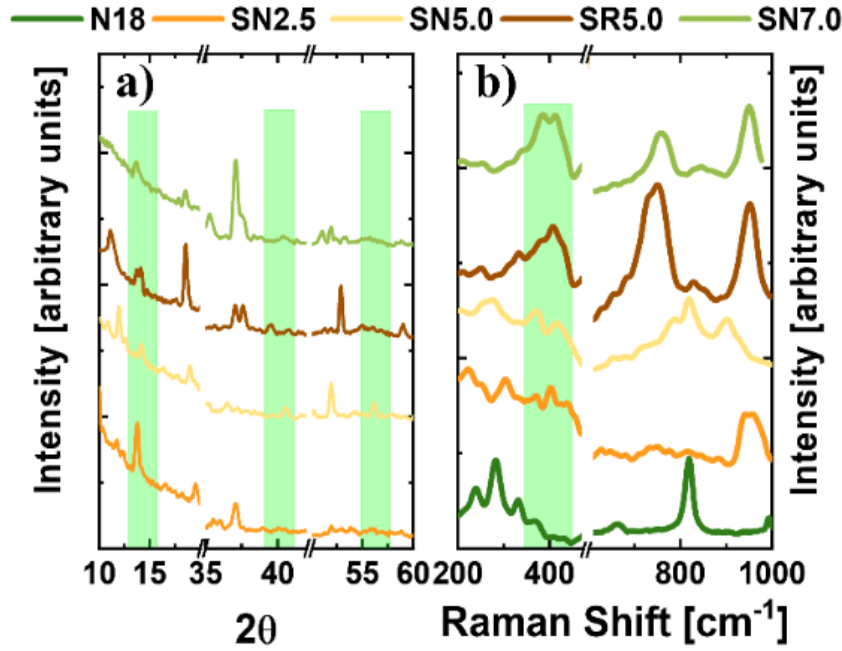


Figure 22 a) XRD spectra of SN2.5 (orange curve), SN5.0 (yellow curve), SN7.0 (dark yellow curve) and SR5.0 (brown curve). b) Raman spectra of different samples are also reported compared with N18 (dark green curve).

The absorption coefficient was calculated using Eq. 1 (see Appendix A), and the Tauc plots (see **Figure 23**) were produced by $(\alpha h\nu)^{1/n}$, with $n=2$ since molybdenum disulphide is considered an indirect bandgap material [156]. Tauc plots of SN2.5, SN5.0 and SN7.0 samples show optical bandgaps around 1.8 eV, higher than of pure MoS₂, which is around 1.2 eV [156]. SR5.0 sample shows a very different value (2.5 eV) from other syntheses. These results suggest that the treatments started from nanostructured materials produce nanostructures closer to MoS₂ than the synthesis obtained starting from Mo-based powder.

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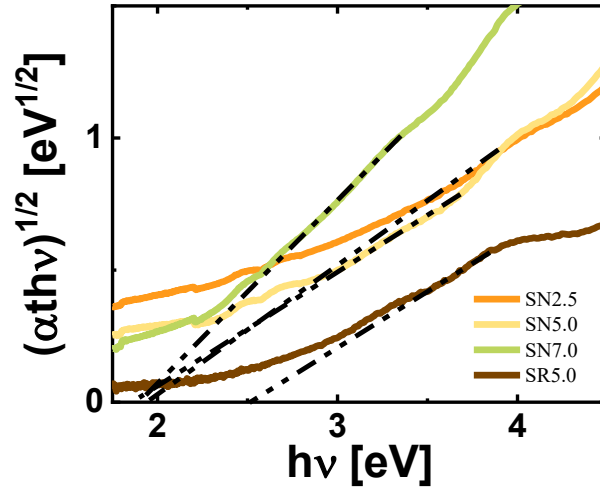


Figure 23 Tauc plots for different samples with the linear fit to extract the optical bandgap.

As just seen, the sample SN5.0 shows interesting features, for this reason we decided to perform other characterizations on it. We employed the Rutherford Backscattering Spectroscopy (RBS, Appendix A) spectrum (see **Figure 24a**), showing the presence of molybdenum at 1.7 MeV, oxygen and sulphur at 0.7 and 1.2 MeV. High-Resolution STEM (Appendix A) images taken on structures from SN5.0 show the crystal lattice typical of 2H-MoS₂ phase (see **Figure 24b-c**).

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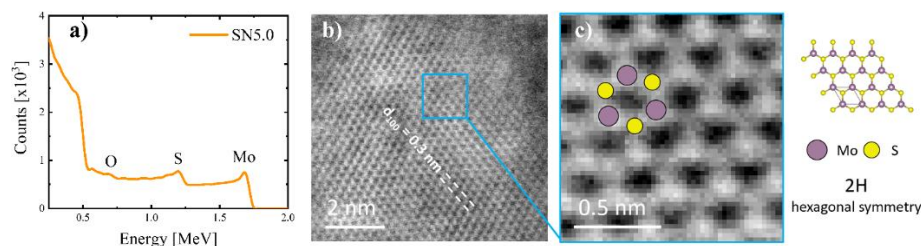


Figure 24 a) RBS spectrum of SN5.0 synthesis confirms the presence of sulphur and oxygen, thanks to the peaks at 0.7 and 1.2 MeV; while the peak at 1.7 MeV is linked to molybdenum.

b) High resolution STEM Z-contrast image of the 2H-MoS₂. c) Zoom-in of the area marked by the blue square, showing the positions of the atoms alongside the atomic model of 2H-MoS₂.

2.3.3 Conclusions

The synthesis of blended material was successfully completed and optimized, seeing the sample SN5.0, its XRD pattern shows three different peaks linked to 2H-MoS₂. The Raman spectrum of this sample clearly shows the in-plane and out-of-plane modes of 2H-MoS₂; here the difference between these two peaks suggests the presence of several layers. Syntheses done employing MoO₃-nanobelts as starting materials report a lower indirect bandgap from UV-Vis measurements, hence closer to pure 2H-MoS₂, than the synthesis executed using directly recycled powder. Further investigations were done on SN5.0 sample, the RBS spectrum was recorded to confirm the presence of sulphur, and typical peak around 1.2 MeV was seen. Also, HRTEM images allow to see the presence of S, and their disposition with hexagonal symmetry.

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2.4 MoS₂-nanosheets

2.4.1 Synthesis procedure

The next step of my work was concerned with the sulfurization of the molybdenum (Mo) based powder, again employing the powder recycled by industrial waste. The hydrothermal treatment was used also for this synthesis due to its cost-effective nature and because it is easy to tune. The followed steps were schematized in **Figure 25**. The starting material was again the Mo-based powder described in Section 2.1; it was magnetically stirred for 30 minutes with thiourea (TU) (Sigma-Aldrich) in 15 mL of deionized water.

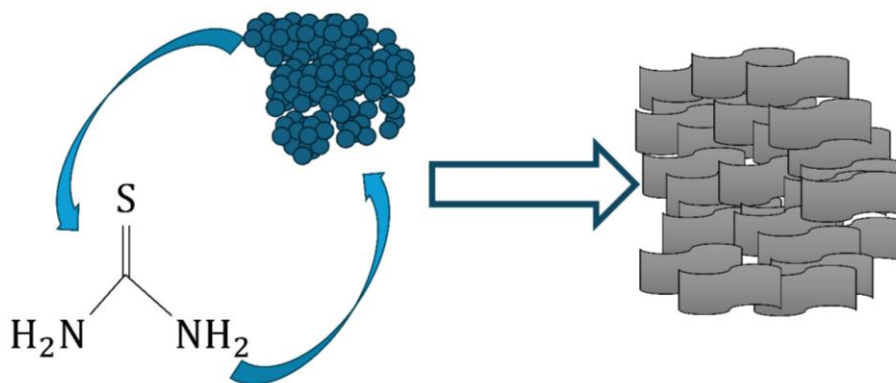


Figure 25 Schematization of the MoS₂-nanosheets synthesis from recycled powder.

The sulfurization was done employing the hydrothermal treatment (HT) which is a cost-effective method easy to tune. The amounts of thiourea and of Mo-based powder were weighted to obtain a S:Mo molar ratio of 2.5. Then, the solution was transferred within a Teflon liner, to perform syntheses processes which differ for temperature and pH. The latter was controlled, through the addition of hydrochloric acid (HCl), starting from a value of about 2.4 to reach a value of 1.1. The solution

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was inserted in an autoclave, which was put in a muffle for 3 h using two temperatures, 180 and 200 °C. In this way, as reported in **Table 3**, four different syntheses were performed, we used the prefix “SR”, which stands for Sulfurized Recycled material, for all the syntheses. The SR_180_2.4 synthesis was performed at 180 °C for 3 hours, the measured pH was about 2.4. Then, we increased the temperature for the hydrothermal treatment up to 200 °C, labelling the sample as “SR_200_2.4”, without varying the pH. The pH was managed for the last two synthesis, decreasing to pH 1.1 adding acid chloride, two syntheses were performed at 180 and 200 °C, SR_180_1.1 and SR_200_1.1, respectively.

After the hydrothermal treatment the solution was cooled at room temperature for 18 h; to conclude the process, the resulted solution was washed and centrifuged with water and ethanol at 6000 rpm three times.

Table 3 Synoptic table for the synthesis.

Name	Temperature [°C]	Time [h]	pH
SR_180_2.4	180	3	2.6
SR_200_2.4	200	3	2.6
SR_180_1.1	180	3	1.1
SR_200_1.1	200	3	1.1

Thanks to the produced syntheses the role of temperature and pH during the growth process will be evaluated, both from morphological and phase point of view.

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2.4.2 Morphological and phase characterization

We optimized the synthesis of nanostructures starting from Mo-based recycled powder; these are not characterized by a well-defined morphology, as shown by high and low magnification (**Figure 12a** and **Figure 12b**, respectively) images. In **Table 3**, the growth parameters of the different syntheses were reported, and the resulting materials were shown in **Figure 26** to highlight the trends of pH value of the synthesis solution and the temperature of the hydrothermal effect. **Figure 26a** and **Figure 26b**, syntheses SR_180_2.4 and SR_180_1.1 respectively, show the effect of the pH, in both cases we can observe the formation of nanosheets. For a more acidic pH, tiny nanosheets were observed, which form more dense clusters of nanostructures. Instead, seeing the **Figure 26c**, hence synthesis SR_200_2.4, the single nanosheets are distinguishable, there is still the trend to form clusters, but they are less dense than the previous case. At the end, we evaluate the combined effect of temperature and pH through synthesis SR_200_1.1 (see **Figure 26d**), where the size of the clusters is closer to the synthesis SR_180_1.1, but they are more distinguishable, like in synthesis SR_200_2.4. SEM images show the effect of the pH value, indeed a reduction of the nanostructure average size can be evaluated; while varying only the temperature an increasing of the size can be seen.

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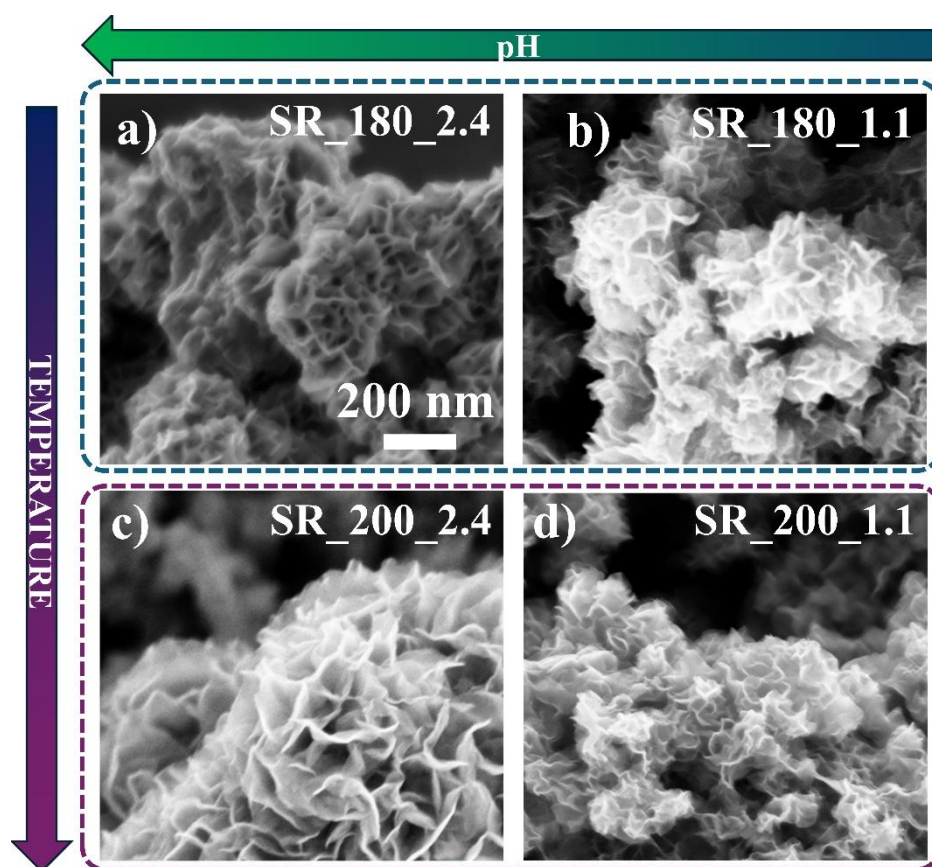


Figure 26 Thanks to this disposition it's possible to observe both the effects of temperature during the hydrothermal process and pH of the solution inserted in the teflon liner; these effects affect the agglomeration of nanosheets as can be seen by SEM images.

Then, to study the composition and structure of the samples, we analysed the samples using TEM analysis. We focused our attention on the samples SR_180_2.4 and SR_200_1.1, to highlight the difference due to the combined effect of pH and temperature on the sample. Two selected area of them, respectively **Figure 27a** and **Figure 27h**, were studied to evaluate the elemental composition and distribution using STEM-EELS analysis (Appendix A), considering S K-edge at 2472 eV

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(red points, **Figure 27c** and **Figure 27m**), Mo L-edge at 2520 eV (green points, **Figure 27b** and **Figure 27l**) and O K-edge at 532 eV (blue points, **Figure 27d**). In some inner areas of SR_180_2.4 sample the O signal is complementary to the S signal (see **Figure 27f** and **Figure 27g**), but also the presence of Mo and S bonds (see **Figure 27e**) was detected, suggesting the presence of both molybdenum sulphides and oxides in the material core, but the more external part is characterized by S dominance, hence MoS₂-nanosheets presence. For SR_200_1.1 no oxygen signals were evaluated, with a great part of S bounded with Mo (**Figure 27i**). Hence, increasing the hydrothermal temperature, the oxygen presence within the nanosheets was undetectable, suggesting a complete conversion to molybdenum sulphide nanostructures.

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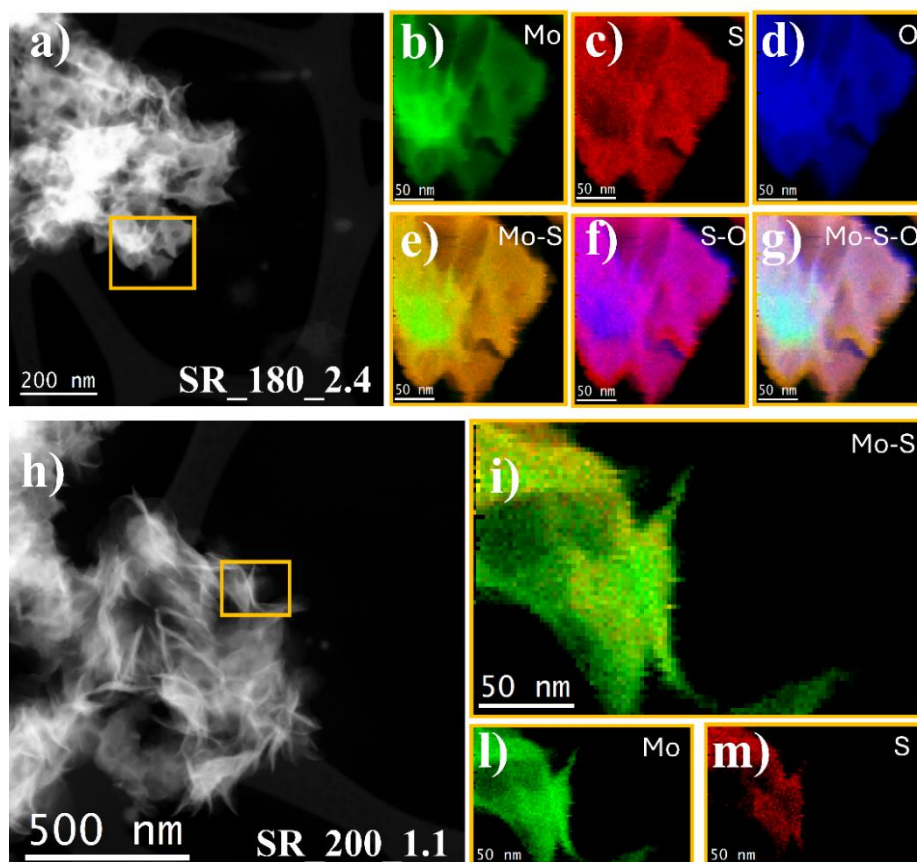


Figure 27 STEM-EELS of syntheses: a-g) SR_180_2.4, in which is highlighted the presence of oxygen and its bonds within the nanosheets; h-m) SR_200_1.1 is reported, in this case no oxygen presence was detected within the nanosheets.

To further verify the presence of MoS_2 , the crystal structures of the two materials were evaluated. **Figure 28a** shows the HRTEM (Appendix A) image of a SR_180_2.4 layer well stacked with an interlayer distance of 0.67 nm (see **Figure 28b**), corresponding to the (002) plane of 2H- MoS_2 [157]. To get more insight into the crystal structure of the MoS_2 nanosheets, we selected a region which shows a single layer. Focusing

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on the area highlighted in green, the Selected Area Electron Diffusion (SAED) pattern was evaluated (see **Figure 28c**). The planes (10-10), (1-100) and (0-110) were reported, which are linked to the hexagonal phase of MoS₂[158], [159]. Moving to the sample SR_200_1.1, reported in **Figure 28d**, we found an interlayer distance of about 0.62 nm along (002), and there was also the possibility of evaluating the lattice parameter in the area delimited by the yellow square, finding a value of 0.27 nm (see **Figure 28e**), usually related to 2H-MoS₂[160], [161]. **Figure 28f** reports the SAED pattern evaluated in the same point, where the spot linked to the basal plane (100) of 2H-MoS₂ is clearly present.

These results confirm the presence of 2H-MoS₂ in both samples, not depending on growth parameters, with a hexagonal structure belonging to the P 63/mmc (194) space group. But they were characterized by different interlayer distances, this parameter can be affected by the number of layers, suggesting that SR_200_1.1 has more overlapped layers than SR_180_2.4, in accordance with what was observed by SEM images.

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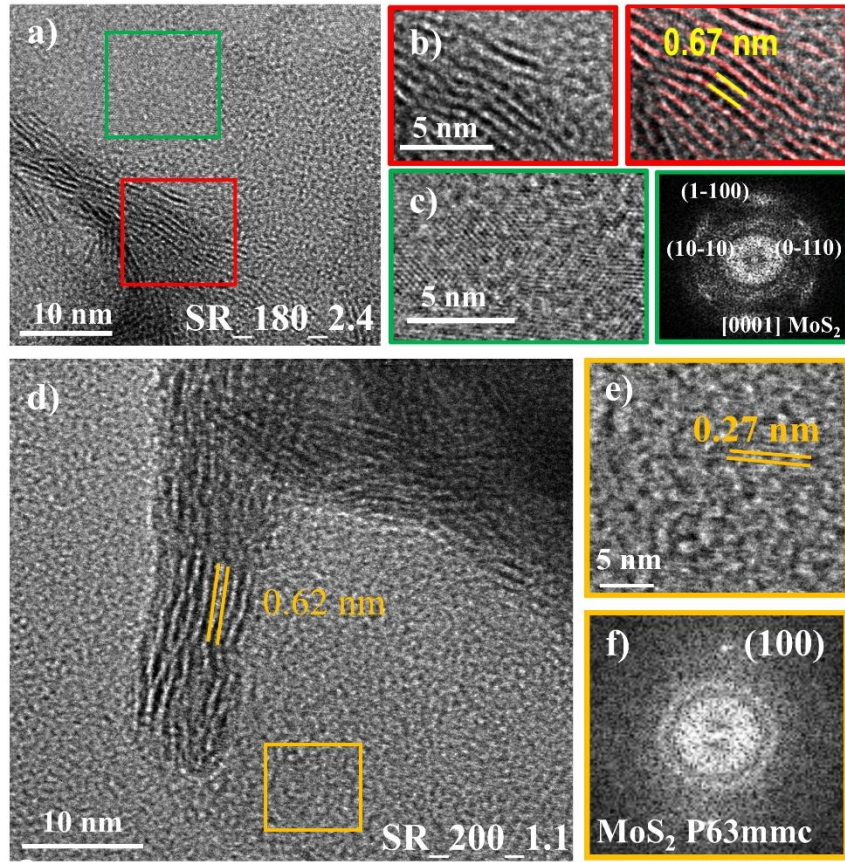


Figure 28 For SR_180_2.4 sample a) HRTEM image was used to study the b) SAED pattern, which shows planes linked to MoS₂ and (highlighted with a green square) and to evaluate the c) interlayer distance (highlighted with a red square) . For the synthesis SR_200_1.1 starting from the d) HRTEM we were able to determine also the e) lattice distance and the presence of the plane (100) from the f) SAED pattern.

For a further study on the crystal structure, the XRD patterns of the samples are reported in **Figure 29**. Materials' nanometric size produces broadening and shifts of the peaks, producing difficulties identifying them, especially at low angles [162]. As seen in our previous work [129], the starting powder is characterized by m-MoO₂ and metallic

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Mo, peaks linked to these species were found in all the samples. In particular, 26.08° , 37.02° , 53.66° , 60.42° and 66.6° which suggest respectively the presence of (-111), (111), (-222), (-131) and (-402) planes of monoclinic MoO_2 (see PDF Card No.:00-076-1807 Quality: C). Firstly, we observe for the samples SR_180_2.4 and SR_200_2.4 a peak around 13.5° that can be linked to the (002) basal plane of 2H- MoS_2 ; it was not detectable for SR_180_1.1, while for the SR_200_1.1 it is strongly left-shifted. The described behaviour in the last two samples suggests a strong strain which affects the material along the (002) direction [160]. The peaks along (002) of SR_180_2.4 and SR_200_1.1 were used to evaluate the crystallite size employing Eq.2 (see Appendix A), finding a reduction from 250 to 35 nm, a decrease also suggested by SEM images. For all samples there are peaks around 27.7° , 33.83° , 37.08° and 49.51° , which can be linked respectively to (100), (101), (103) and (105) planes of metallic 2H- MoS_2 ; the presence of more peaks at higher angles suggests a strong nanostructurization of the material. This fact is also supported by the peak at 58.6° , associated with (110) of 2H- MoS_2 planes (see PDF#73-1508) [163].

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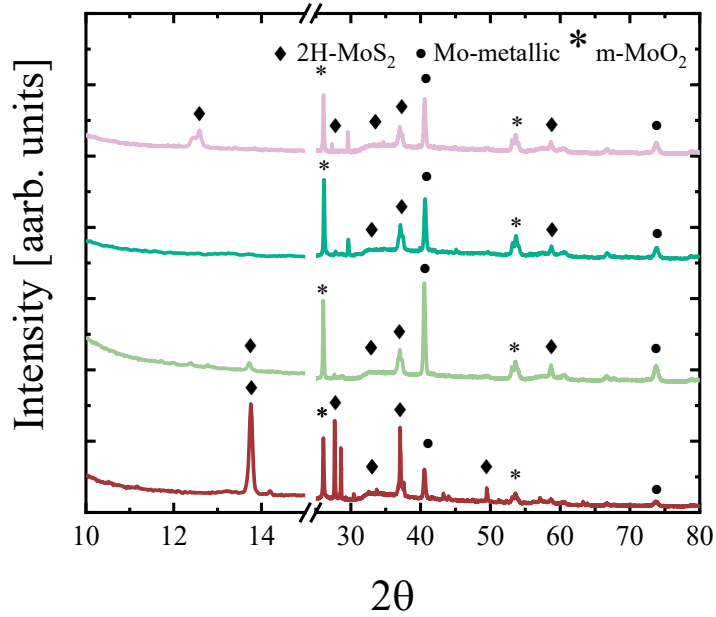


Figure 29 The crystal structures of samples were also studied using XRD patterns, here the peaks are assigned to 2H-MoS₂, metallic Mo and monoclinic MoO₂.

To further study the possible presence of different Mo-species, other techniques, like Raman Spectroscopy (Appendix A), were performed. **Figure 30** shows Raman spectra of the materials with many different peaks. The peaks around 370 and 400 cm⁻¹ suggest the presence of 2H-MoS₂, since they are linked to E_{2g}¹ and A_{2g}, in-plane and out-of-plane phonon modes, respectively [153]. The presence of grain boundaries induces a peak broadening because edge-sites can be considered as defects concerning pure crystalline structures [155]. Reducing nanostructures size the strains in the materials increase, producing defects, which have another consequence for MoS₂, the downshift of E_{2g}¹ and the upshift of A_{2g} with respect to the theoretical positions [164]. The Δ distance between these two peaks is calculated and reported in **Table 4** for each sample, it is directly proportional to the number of

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layers [165]; hence, seeing its passage from SR_180_2.4 to SR_200_1.1, we are observing an increase of MoS₂ layers, which is in accordance with the reduced interlayer distance seen in the two samples through HRTEM analysis [153].

Table 4 Synoptic table for peaks linked to in-plane and out-of-plane modes; it is also reported the distance between the peaks.

Sample	E _{2g} ¹ [cm ⁻¹]	A _{2g} [cm ⁻¹]	Δ [cm ⁻¹]
SR_180_2.4	372	400	28
SR_200_2.4	377	403	26
SR_180_1.1	372	398	26
SR_200_1.1	369	400	31

In the Raman spectrum, it is also possible to observe the peaks around 220 and 450 cm⁻¹, which correspond to the first and the second order of longitudinal acoustic modes of 2H-MoS₂ [164]. XRD patterns and Raman spectra confirm the presence of layered 2H-MoS₂. Controlling both temperature and pH, we were able to handle the number of layers, hence the interlayer distance of the material.

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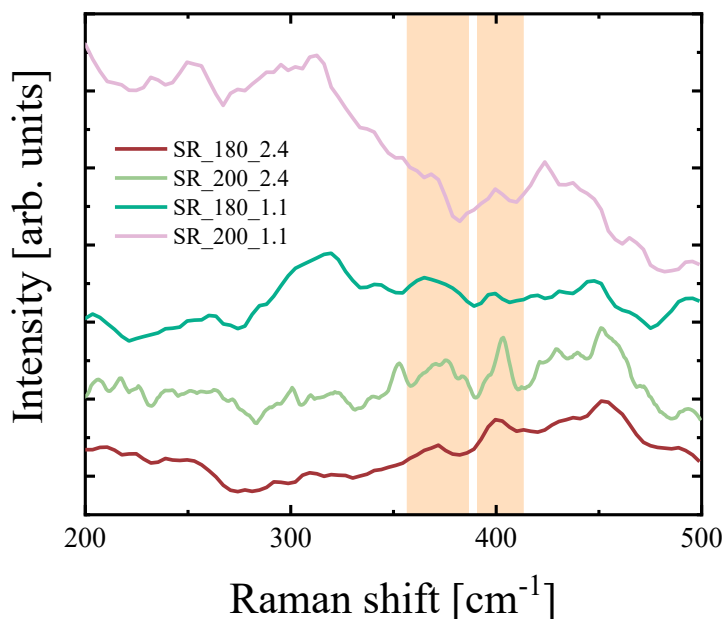


Figure 30 The Raman spectra of the materials are reported here, the bands around the 375 and 400 cm^{-1} are highlighted.

The chemical composition of the sample surfaces was investigated by X-ray photoelectron spectroscopy (XPS, Appendix A). For each of the four samples analyzed - SR_180_2.4, SR_180_1.1, SR_200_2.4, and SR_200_1.1 - wide scan spectra and high-resolution (HR) spectra in the Mo 3d and S 2p binding regions were acquired, along with surface elemental compositions obtained from quantitative analysis.

The deconvolution of the Mo 3d region (see **Figure 31a–d**) reveals three distinct chemical states for all samples: a component attributable to Mo in the sulfide form (green line), associated with the 2H-MoS₂ phase; a second component compatible with Mo(IV) oxide (MoO₂, blue line); and a third contribution assigned to Mo(VI) oxide (MoO₃, orange line), confirming the presence of these three species. From **Figure 31a** to **Figure 31b** and **Figure 31c**, the MoO₃ peaks are still present, while,

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combining the effect of pH and temperature, its signal strongly decreases, suggesting a better sulfurization of the Mo-based starting material.

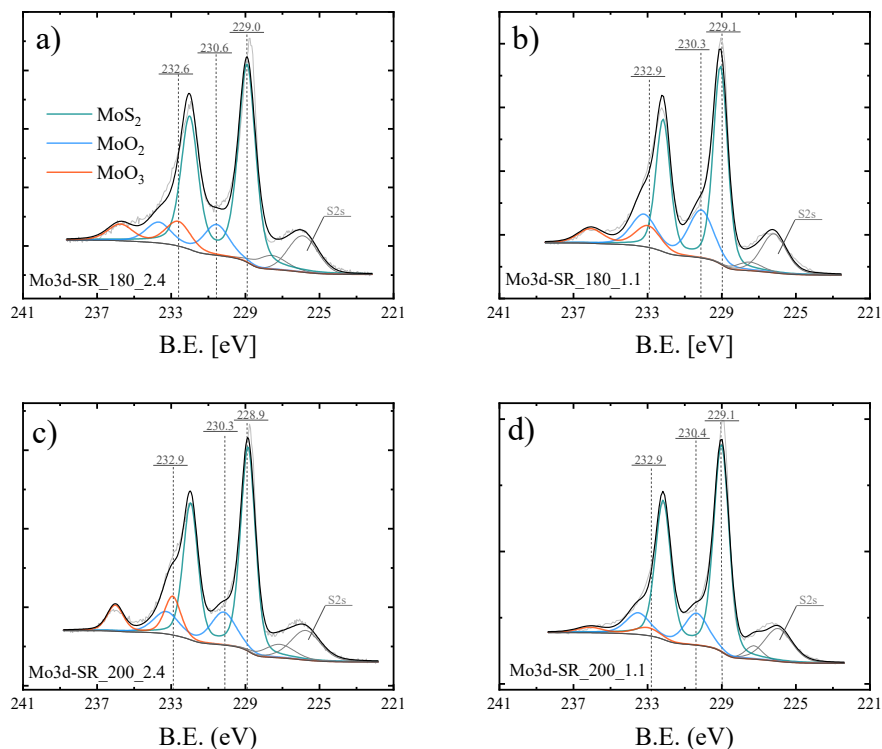


Figure 31 XPS spectra in the Mo 3d region with peak deconvolution for: a) SR_180_2.4, b) SR_180_1.1, c) SR_200_2.4, and d) SR_200_1.1.

The assignment of the peaks to MoO_2 was complicated to do for the XPS analysis, indeed in the same positions there are also the 1T- MoS_2 ones; unfortunately, this phase share XRD and Raman peaks with the 2H- MoS_2 one. The shifts seen in the spectra, due to the presence nanostructures in the material, also complicated the evaluation of the presence of the 1T- MoS_2 within the samples. A further analysis was performed, to study the possible presence of 1T- MoS_2 in the material,

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indeed the samples were studied using X-ray Absorption Near Edge Structure (XANES, see Appendix A) technique, the profiles are reported in **Figure 32a**. Different works report this analysis, in particular Cai and colleagues study the transformation of 2H-MoS₂-nanosheets in a mixed phase between 1T and 2H (see **Figure 32b**), also comparing the electrochemical behaviour of the samples to highlight the differences. The experimental spectra reported in **Figure 32a** have a shape closer to 1T@2H-MoS₂-nanosheets (see **Figure 32b**), suggesting the presence also of 1T-MoS₂ within the sample [166]. The absence of the peak at 20100 eV can be linked to the nanosheets morphology.

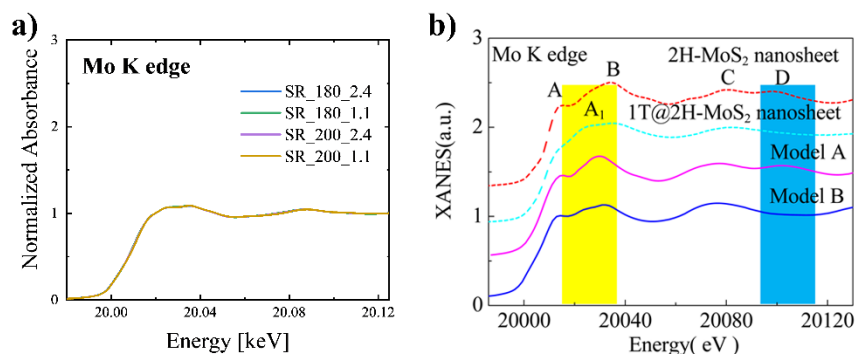


Figure 32 a) The XANES spectra of the samples are overlapped to perform a comparison, no relevant distinction are shown; b) reference spectra from the work of Cai et al. [166].

Indeed, the above conclusions are corroborated by the Fourier transformed (FT) of the EXAFS spectra reported in **Figure 33**, where again features at 1.6 Å, 2.0 Å and 2.4 Å in r-space consistent with the presence of Mo-O, Mo-S and Mo-Mo scattering. Here again the data show an apparent increase in Mo-S scattering for SR_180_1.1 and SR_200_2.4. Interestingly, however little change is visible for the Mo-O feature at 1.6 Å, yet significant reduction in the Mo-Mo scattering is observed at 2.4 Å for SR_180_1.1 and SR_200_2.4. The typical peak at 2.0 Å linked to 2H-MoS₂ is clearly distinguishable [167], while the

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second one, usually around 2.6 Å, is incorporated with the one due to some residual of the starting material.

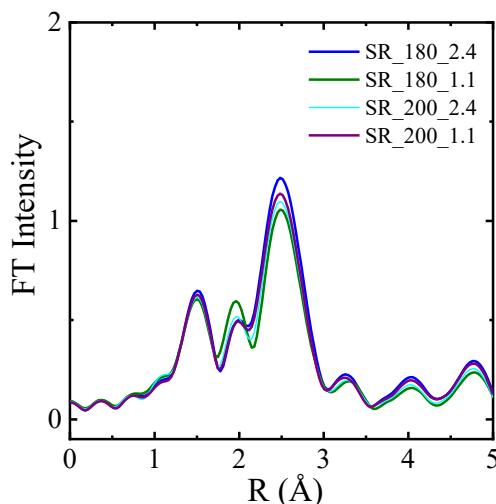


Figure 33 FT spectra (k-range 3 -12 Å⁻¹, Hanning window dk=1).

2.4.3 Conclusions

Thanks to SEM images we observed the presence of agglomerated nanosheets, and varying temperature and pH value of the solution before the hydrothermal treatment there is a decreasing of nanostructures size, also recording an improvement of clusters of nanostructures especially in the samples in which the pH value before the hydrothermal treatment was controlled and fixed to 1.1. STEM-EELS measurements highlighted how no oxygen traces are detected within the nanosheets, increasing the hydrothermal temperature and shifting to more acidic pH values. HRTEM images allowed us to focus our attention on the interlayer distance, from SR to SRT200PH1.1 there

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is a decrease in this distance, suggesting an increase in the number of layers.

XRD patterns show the global composition of the material, and the variation of the peaks linked to the basal plane (002) suggests the presence of nanostructures, such as the presence of broadened peaks linked to (100) and (101). These trends are also confirmed by Raman measurements, where a left shift of E_{2g}^1 peak suggests an important strain of in-plane modes, and again we observe broadened peaks due to the presence of nanostructures.

XPS data indicate that the SRT200PH1.1 sample has the highest Mo(IV) sulfide fraction and the lowest Mo(VI) oxide content, suggesting a lower degree of surface oxidation compared to the other samples. This feature is consistent with the observed improved electrochemical performance, in agreement with previous studies showing that the presence of MoO_3 on the surface reduces electronic conductivity and charge storage efficiency. Molybdenum-to-sulfur ratios close to the stoichiometric value expected for MoS_2 confirm the effectiveness of the sulfidation process. XANES spectra highlight the presence of 1T- MoS_2 in the samples.

Chapter 3. Mo-based nanocatalysts for water splitting

3.1 Overview of Mo-based nanocatalysts

Thanks to their multiple oxidation states, transition metal oxides (TMOs) are a promising class of materials for new technologies [48]. Among TMOs there are molybdenum oxides, which possess many features like Earth abundance and low cost [135]. Moreover, molybdenum (Mo) is absent from the CRMs list published in 2023, whereby the use of these elements and their compounds has attracted greater interest [168].

Mo-based materials have different promising features, for instance, they can be promising materials for water splitting applications thanks to their bands positions (see **Figure 34**). Indeed, while MoO_3 has a valence band close to the energy level of the Oxygen Evolution Reaction [147], the MoS_2 has the position of the conduction band close to Hydrogen Evolution Reaction [169].

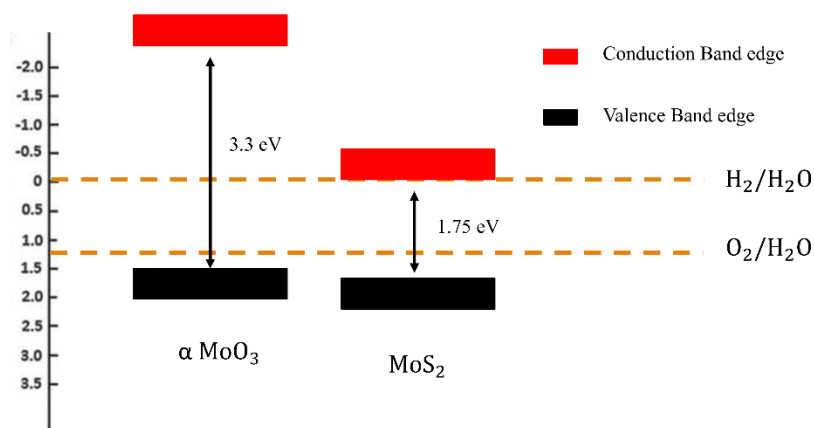


Figure 34 Conduction and Valence bands positions of Mo-based materials.

Mo-based nanocatalysts for water splitting

MoO₃ synthesis is widely studied, and different procedures were proposed using molybdenum salts as starting reagents [144], [170], [171]. Mo oxides are promising electrocatalysts for OER in different electrolyte environment, they are also applied for overall water splitting cell [172], [173]. MoO₂ and MoO₃ are the most diffused molybdenum oxides, and the orthorhombic molybdenum trioxide (α -MoO₃) is the most stable phase used for many applications. The molybdenum oxide has a stable structure consisting of a bilayer structure oriented along the [010] direction, which corresponds to the c-axis. MoO₃ is a n-type semiconductor, with a bandgap of about 3.0-3.3 eV (depending on the material size and shape) [146], [147], [174]. It is used as one-dimensional nanostructures for most applications since this morphology can enhance electrocatalytic performances thanks to the increase of the specific surface area [175]. For instance, Kim et al. reported α -MoO₃/CFP for OER in 1M KOH with an overpotential of 910 mV and a Tafel slope of 206 mV dec⁻¹ calculated at 10 mVcm⁻² [173]. In another work, Li and his colleagues reported an overpotential of 630 mV and a Tafel slope of 110 mV dec⁻¹ at 10 mVcm⁻² for a MoO₃/glassy carbon [172], while Zhang et al. obtained a porous MoO₃ with an overpotential of 450 mV and a Tafel slope of 125 mV dec⁻¹ [176]. Knowing the previous works we decided to test the synthesised MoO₃-nanobelts for OER application.

Also, transition metal sulphides (TMSs) have attracted much interest in the last decades for water splitting applications, like molybdenum disulfide (MoS₂), which was widely studied alone and within different compounds [177]. MoS₂ is usually reported with a few-layered structure, its features and electronic performances strongly depend on the number of layers [156]. Different works reported MoS₂-based electrodes, for instance, Lai et al. obtained few-layered nanosheets of MoS₂ with an overpotential of 540 mV and a Tafel slope of 130 mV dec⁻¹ 0.5 M H₂SO₄ [178]. Liu and his colleagues reported a synthesis of

Mo-based nanocatalysts for water splitting

2H-MoS₂, it was applied for HER with an overpotential of 354 mV and a Tafel slope of 189 mVdec⁻¹, while Duraisamy et al. used a hydrothermal treatment to synthesise nanosheets of MoS₂/MoO₃ obtaining an electrode with 208 mV and 94 mVdec⁻¹ respectively for overpotential and Tafel slope [80].

In Section 2.2 and Section 2.3 two syntheses were described, respectively MoO₃-nanobelts and mixed MoS₂/MoO₃-nanostructures. Morphology and phase of these materials were widely studied in the previous chapter, here a study of the electrocatalytic behaviour is presented, hoping to show a new way for the employment of recycled materials. At the end of this chapter, a possible application for the synthesised electrodes is reported, indeed they were used to assemble an overall water splitting cell in alkaline electrolyte.

3.2 MoO₃-nanobelts for Oxygen Evolution Reaction

In this section an electrochemical comparison of molybdenum oxides N0, N7, N14 and N18 (see **Table 1**) samples is reported. The preparation of the electrodes for this purpose is reported in Appendix B. In particular, molybdenum oxides samples were tested for Oxygen Evolution Reaction (OER) measurements. According to literature they have features, like band positions [179], which favour the employment to specific applications than other ones [172].

First, the Linear Sweep-Voltammetry (LSV) measurements were executed, then Electrochemical Impedance Spectroscopy (EIS) spectra of the samples were collected (see Appendix C) at the OER potential to evaluate the uncompensated resistance, which was used to correct the LSV thanks to the Eq.4 (see Appendix A). The electrochemical OER performances of MoO₃ nanobelts were studied by LSV, as reported in

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Figure 35a, after the iR correction. The curves of bare GP and Mo-based starting powder (light blue and dark brown curves, respectively) are also reported to evidence the substrate and nanostructures' presence effect. After an initial plateau, in which no current flows between the electrodes, the OER mechanism starts and the current rapidly increases with the potential increase, with features that depend on the morphology, crystallinity and stoichiometry of MoO₃ nanostructures. To compare the efficiency of all the electrodes, the overpotential (η) at 10 mA cm⁻² was extracted from LSV curves and reported in **Table 5**.

It should be noted that the Mo-based catalyst amount is 0.9 mg cm⁻² for all the samples. The lowest overpotential is obtained for N18 sample (324 mV, dark green curve), well lower than that of the GP substrate and Mo-based starting powder (360 and 340 mV, respectively). For the N0 sample (light brown curve) a promising overpotential (326 mV) is obtained, then, by reducing the pH, the overpotential increases until to reach 362 mV for the N7, and then decreases, reaching the minimum overpotential (324 mV) for N18 sample. Raman analysis (see Section 2.2) shows the presence of sub-stoichiometric molybdenum oxides characterized by oxygen vacancies, these defects can lead to better OER performances, as just reported in the literature [136]. Then, when the stoichiometric structure is obtained (N7 and N18 samples), the OER performances depend on the morphology and crystallinity, reaching the best response for the N18 sample (only α -MoO₃).

Tafel analysis was carried out to determine the Tafel slope which allows us to achieve a deeper knowledge of the charge transport mechanism involved during the OER process [180]. In **Figure 35b** the Tafel plots for the different syntheses are displayed, with a magnification around 10 mA cm⁻²; the lower Tafel slope belongs to N18 and N14 samples, which are 45 and 50 mV dec⁻¹, respectively, while N7 and N0 have higher values, as reported in **Table 5**. While N18 and N0 samples show similar low overpotential, they possess quite different Tafel slopes,

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highlighting a different OER kinetics. N18 sample has by far a lower Tafel slope, leading to an outperformance at a higher current.

The electrocatalytic activity of the samples was also studied evaluating the mass activity using Eq.5 (see Appendix A). For N18, N14 and N7 samples the mass activity at 10 mA cm^{-2} is around $1.2\text{-}1.3 \text{ } 10^{-2} \text{ A mg}^{-1}$. The N0 and R0 mass activity ($1.0 \text{ } 10^{-2} \text{ A mg}^{-1}$) are lower than the previous ones (see **Table 5**).

Table 5 Summary of electrochemical OER parameters of MoO_3 nanostructures

Name	η [mV]	Tafel Slope [mV dec ⁻¹]	Mass Activity [$10^{-2} \text{ A mg}^{-1}$] I	E_g [eV]
N18	324	45	1.2	3.3
N14	342	50	1.3	3.3
N7	362	113	1.3	3.3
N0	326	79	1.0	3.5
R0	340	45	1.0	3.5

Mo-based nanocatalysts for water splitting

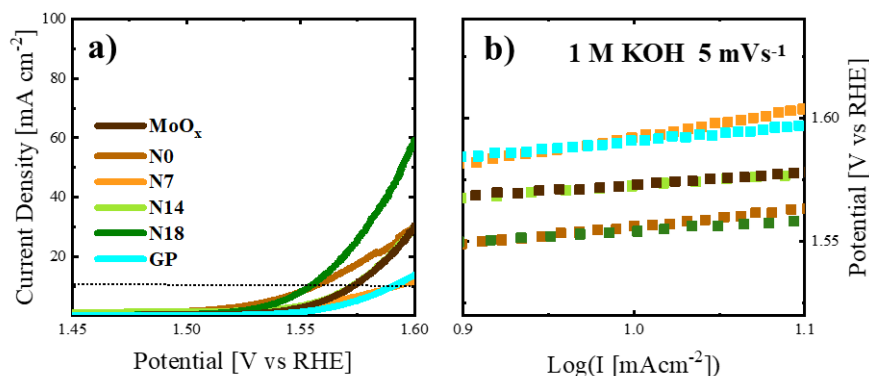


Figure 35 a) LSV curves after iR correction using EIS measurements (see Appendix C) and b) Tafel Slopes of synthesis N0 (light brown curve), N7 (orange curve), N14 (light green curve) and N18 (dark green curve) compared to Graphene Paper (light blue curve) and Mo-based powder (dark brown curve). The measurements were done in 1 M KOH with a scan rate of 5 mV s^{-1} .

The band position of MoO_3 is favourable for OER application, but also the nanobelt growth along (0k0) produces many edge sites along other directions, and these can act as active sites for the adsorption mechanism of OH^- , justifying the lower Tafel slope reported for N18. On the other hand, higher values of Tafel slopes are accounted to a predominance of recombination mechanism at the surface, as reported in literature [180].

N18 shows the best performances for OER, hence we decided to test its durability as shown in **Figure 36** (green curve). The sample shows excellent stability for 15 h.

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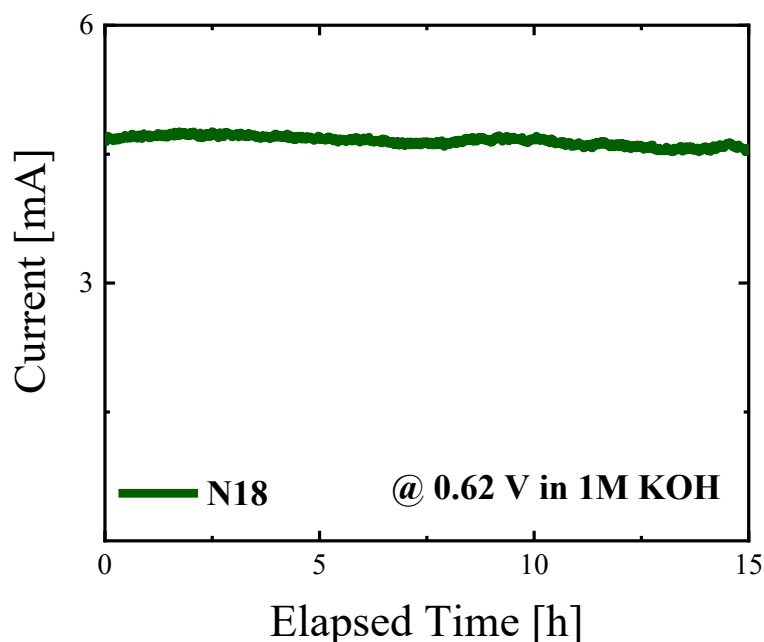


Figure 36 The durability curves of N18 sample.

In **Figure 37** the overpotential and Tafel slope of N18 and R0 samples are compared with literature data of MoO_3 -based catalysts for alkaline OER (see **Table 6**). A remarkable improvement of both overpotential and Tafel slope respect to the literature data is evident, despite the use of industrial waste powder as starting material. In **Table 6** mass activity values are also reported, it is possible to observe how the synthesized nanostructures have values comparable with the state-of-the-art.

Mo-based nanocatalysts for water splitting

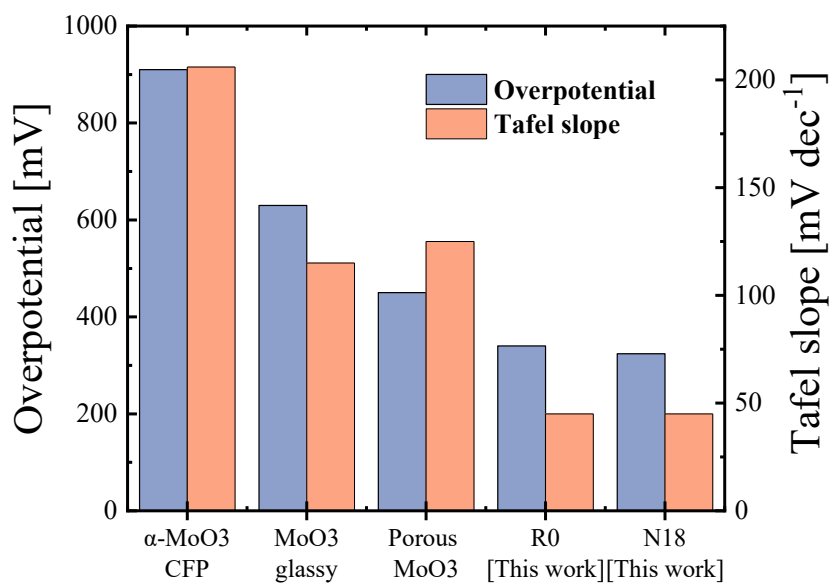


Figure 37 MoO₃-nanobelts are compared with similar MoO₃-based catalysts active for OER application measured in 1M KOH, with the overpotential evaluated at 10 mV cm⁻².

Table 6 Comparison of catalytic parameters of MoO₃-based materials, at 10 mA cm⁻² with 1 M KOH electrolyte.

Catalyst	η [mV]	Tafel Slope [mV dec ⁻¹]	Mass Activity [10 ⁻² A mg ⁻¹]	Catalyst loading [mg]	Reference
α -MoO ₃ /CFP	910	206	1.00	0.10	[173]
MoO ₃ /glassy carbon	630	115	5.0	0.04	[172]
Porous MoO ₃	450	125	5.0	1.40	[176]
Mo-based powder (R0)	340	45	1.0	1.00	This work
MoO ₃ -nanobelts (N18)	324	45	1.2	0.80	This work

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3.3 MoS₂/MoO₃-nanostructures for Hydrogen Evolution Reaction

Mo-based materials are a promising class for electrocatalysts. While Mo-oxides are used for OER applications, Mo-sulphide based ones can be employed for Hydrogen Evolution Reaction (HER) applications [178]. Blended materials attracted much interests, indeed the formation of heterojunctions seems to enhance the electroactivity of the material [80]. The electrodes to perform the electrochemical characterization are prepared as reported in Appendix B. Again, EIS spectra (see Appendix C) were collected to evaluate the uncompensated resistance of the samples, to perform the iR correction using Eq.4 (see Appendix A).

The electrochemical characterization of MoS₂/MoO₃ as HER electrocatalysts can be appreciated from LSV curves reported in **Figure 38a**, after iR correction. The N18 (dark green curve) is shown to highlight the beneficial effect of sulfurization. All the measurements are characterized by an initial plateau followed by the HER onset. In **Table 7** in the ESM the electrochemical parameters of the samples are resumed, focusing on 10 and 25 mA cm⁻². The N18 shows a very high overpotential at 10 mA cm⁻² (608 mV), followed by SR5.0 sample (444 mV). SN2.5 and SN5.0 samples show a significant decrease of the overpotential (290 mV and 205 mV, respectively), while it slightly increases with SN7.0 sample (230 mV).

In **Figure 38b** the Tafel plot at 10 mAcm⁻² are reported. The extracted values were reported in **Table 7**, and the lowest Tafel slope was obtained for SN7.0 (91 mVdec⁻¹), and SN5.0 (94 mVdec⁻¹), while for SN2.5 it is 117 mVdec⁻¹. The Tafel slopes reflect the slowest mechanism that occurs during HER, and for these samples the Tafel slope values can be accounted to a Volmer step as rate determining step (RDS) [180].

Mo-based nanocatalysts for water splitting

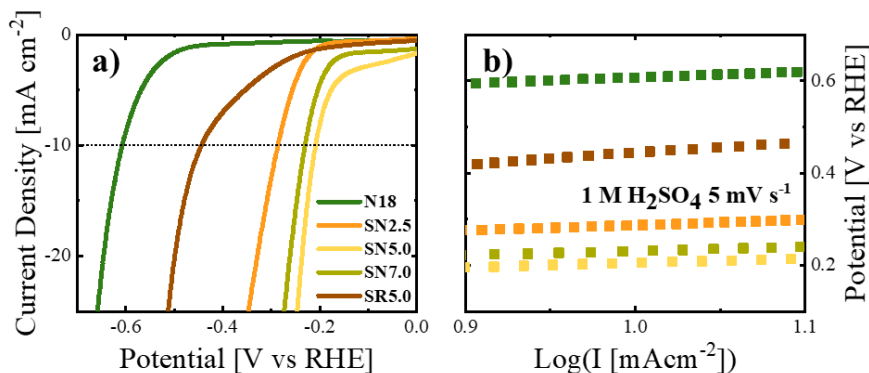


Figure 38 a) LSV curves of MoO₃ nanobelts (N18, dark green curve) compared with SN2.5 (orange), SN5.0 (light orange curve), SN7.0 (dark yellow curve) and SR5.0 (yellow curve) in 1 M H₂SO₄; b) Tafel plot of the different samples. The measurements were done in 1M H₂SO₄ with a scan rate of 5 mVs⁻¹. The overpotentials was calculated at 10 mA cm⁻².

The trend of performances at 25 mA cm⁻² is the same observed at lower current density and SN5.0 is still the best sample. At 25 mA cm⁻² SN5.0 records an overpotential two times lower than SR5.0.

For all the samples, the electrocatalytic activity was also evaluated through the mass activity estimate, for both 10 and 25 mA cm⁻². For instance, the mass activity values were reported in **Table 7**, SN5.0 shows mass activity values of 0.3 10⁻² A mg⁻¹, 0.8 10⁻² A mg⁻¹, respectively at 10 and 25 mA cm⁻².

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Table 7 Summary of calculated electrochemical performances of nanostructures.

Name	Overpotential [mV @10 mA cm ⁻²]	Tafel slope [mVdec ⁻¹ @10 mA cm ⁻²]	Mass Activity [10 ⁻² A g ⁻¹ @10 mA cm ⁻²]	Overpotential [mV @25 mA cm ⁻²]	Tafel slope [mVdec ⁻¹ @25 mA cm ⁻²]	Mass Activity [10 ⁻² A g ⁻¹ @25 mA cm ⁻²]
N18	608	128	1.3	658	128	3.3
SN2.5	290	117	0.4	347	205	1.0
SN5.0	208	94	0.3	247	98	0.8
SN7.0	230	91	0.2	274	127	0.6
SR5.0	444	190	1.2	512	130	3

SN5.0 was also measured for long-term stability measurements, showing a fair stability for 15 h, especially after the starting 8 ones (see **Figure 39**), orange curve).

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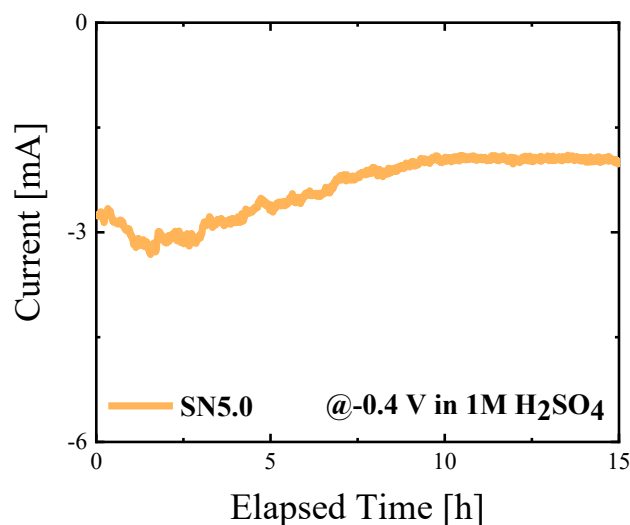


Figure 39 The durability curves of SN5.0 (orange curve).

The best sample, the SN5.0 one, was also measured in 0.5 M H₂SO₄. The material displays an overpotential of 280 mV and a Tafel Slope of 129 mV dec⁻¹ evaluated from LSV curve.

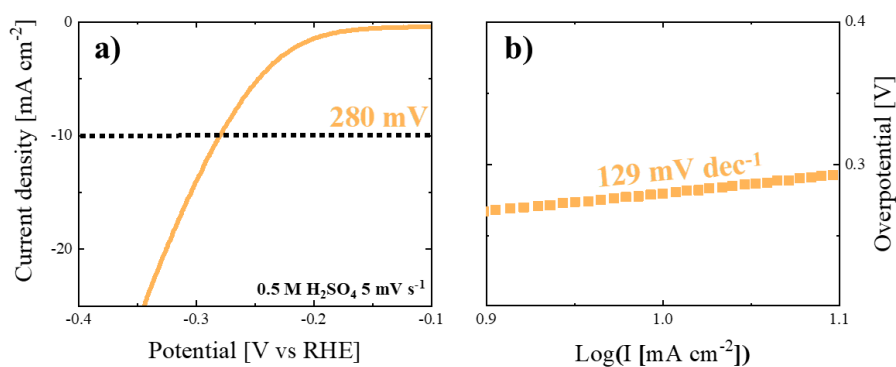


Figure 40 a) LSV curve after iR correction of SN5.0 sample in 0.5 M H₂SO₄ is reported, the overpotential calculated at 10 mA cm⁻² is shown; b) Tafel slope of the sample is also evaluated starting from LSV curve.

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Thanks to the previous measurement, a comparison with other works in the literature was possible. Indeed, Molybdenum disulfide was widely treated in the literature, this fact allow us to compare our results with the state-of-the-art, as reported in **Figure 41** and listed in **Table 8**. It is possible to observe how our sample possesses a lower overpotential than pure MoS₂ [152] and other alloys. SN5.0 sample was obtained after a sulfurization of MoO₃. Actually, the bandgap of MoS₂ is smaller than that of MoO₃, according to literature [177] and shown by optical band gap calculations, and moreover the conduction band is closer to the H⁺/H₂ level for water splitting, representing a great advantage for HER. Hence, thanks to band position more electrons are available for HER than MoO₃ case.

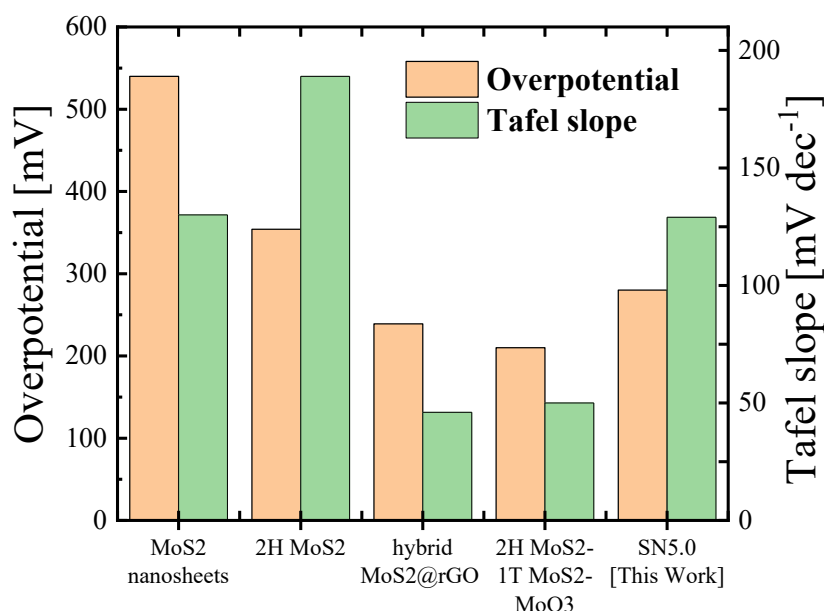


Figure 41 f) MoS₂/MoO₃-nanostructures are compared with MoS₂-based catalysts active for HER application in 0.5 M H₂SO₄.

Mo-based nanocatalysts for water splitting

Table 8 Comparison of catalytic parameters of MoS₂-based materials, at 10 mA cm⁻² in 0.5 M H₂SO₄ electrolyte.

Catalyst	Overpotential [mV]	Tafel slope [mV dec ⁻¹]	Mass activity [10 ⁻² A mg ⁻¹ @10 mA cm ⁻²]	Catalyst Loading [mg cm ⁻²]	Reference
Few-layered MoS ₂ nanosheets	540	130	0.3	3.57	[178]
2H MoS ₂	354	189	0.3	3.00	[152]
MoS ₂ @rGO hybrid	239	46	2.5	0.40	[181]
2H MoS ₂ - 1T MoS ₂ - MoO ₃	210	50	3.5	0.28	[80]
2H MoS ₂ /MoO ₃	280	129	0.28	3.60	This work

3.4 Overall water splitting cell

As proved, the synthesized electrocatalysts based on MoO₃-nanobelts and MoS₂/MoO₃-nanostructures are active for OER and HER, respectively. In the first case the performances are better than the state-of-the-art, while in second one results comparable with other works were obtained. In Section 1.2.2 it was presented how alkaline electrolyte is a promising choice for Overall Water Splitting (OWS) cell application according to the literature [182], [183]. Once characterized the nanostructures for both OER and HER, the goal to employ them to assemble a OWS with alkaline electrolyte was fixed. To do what said, we characterized the SN5.0 sample in alkaline electrolyte (1 M KOH). In **Figure 42a** the LSV curve of SN5.0 is reported, with a promising overpotential of 370 mV in alkaline electrolyte (1 M KOH), it was evaluated also the Tafel slope of 43 mV dec⁻¹ at 10 mV dec⁻¹ (**Figure 42b**).

Mo-based nanocatalysts for water splitting

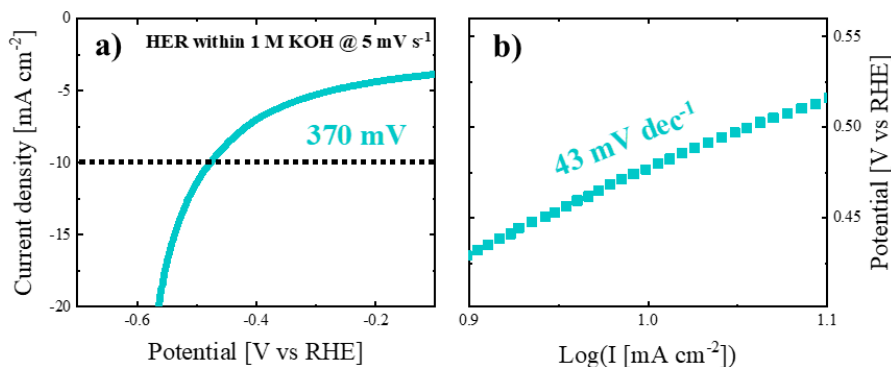


Figure 42 a) LSV curve of SN5.0 sample in 1 M KOH with a scan rate of 5 mV s^{-1} , an overpotential of 370 mV is reported; b) the Tafel slope of the sample calculated at 10 mV cm^{-2} .

Thanks to this characterization, the OWS cell was assembled as reported in **Figure 43**. The sample N18, based on MoO_3 -nanobelts, was employed as anode, while SN5.0, characterised by $\text{MoS}_2/\text{MoO}_3$ -nanostructures, is used as cathode in alkaline electrolyte 1M KOH.

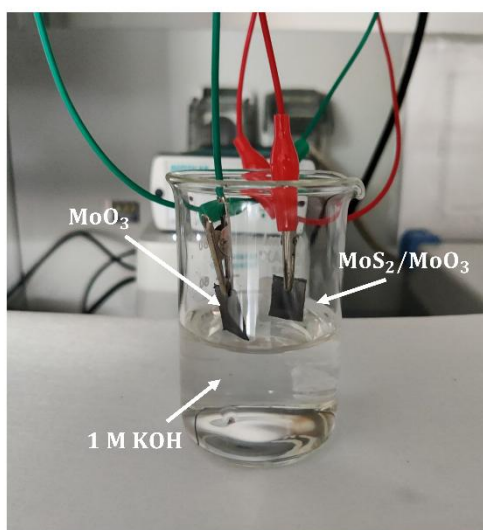


Figure 43 Setup of the OWS cell, in which are highlighted anode (MoO_3) and cathode ($\text{MoS}_2/\text{MoO}_3$).

Mo-based nanocatalysts for water splitting

The LSV of the assembled OWS cell was recorded in 1M KOH with a scan rate of 10 mVs^{-1} . The proof-of-concept device shows a potential of about 1.9 V and a Tafel slope of 57 mV dec^{-1} , **Figure 44a** and **Figure 44b** respectively.

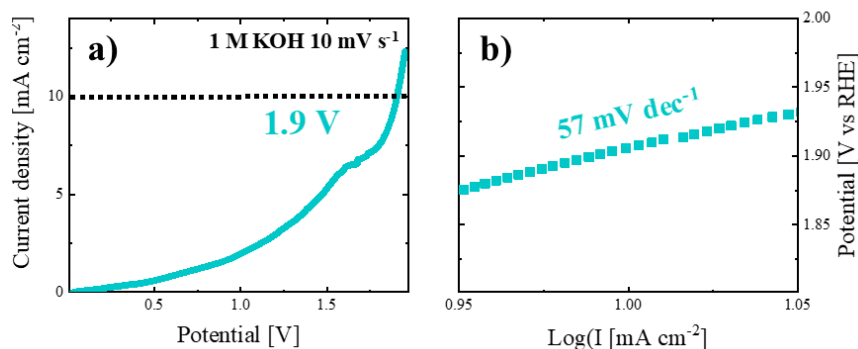


Figure 44 a) LSV curve of the OWS cell composed by MoO_3 (anode) and $\text{MoS}_2/\text{MoO}_3$ (cathode); b) the Tafel slope of the OWS calculated at 10 mV cm^{-2} .

3.5 Conclusions

$\alpha\text{-MoO}_3$ nanobelts produced at acidic pH showed promising OER features in alkaline conditions (overpotential of 324 mV, Tafel Slope of 45 mV dec^{-1} and mass activity of $1.2 \cdot 10^{-2} \text{ A mg}^{-1}$, at 10 mA cm^{-2}). It should be noted that our $\alpha\text{-MoO}_3$ nanobelts, produced by recycled industrial waste, display catalyst performances higher than other Mo oxide-based catalysts present in the literature.

To produce effective HER electrocatalysts we developed a hydrothermal synthesis in Thiourea solution, to reduce and sulfurize the $\alpha\text{-MoO}_3$ nanobelts obtained above. Actually, by optimizing the Thiourea/nanobelts ratio, a mixture of molybdenum sulphide and oxides (MoO_3 and MoO_2) is achieved with irregular nanostructures

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debris (100-300 nm in size). The best HER performances in acidic condition (overpotential of 208 mV, Tafel slope of 94 mV dec⁻¹ and mass activity of 0.3·10⁻² A mg⁻¹, at 10 mA cm⁻²) were found to be comparable or better than literature data with Mo-based catalysts with similar composition.

A OWS cell was successfully tested in alkaline electrolyte, showing a potential of 1.9 V and a Tafel slope of 57 mV dec⁻¹. This result is still far to be competitive with other works in the literature[184], nevertheless the results offer a good first step for future optimization on this device, allowing to assemble competitive devices starting from recycled materials. Indeed, these data show a sustainable route, as schematized in **Figure 45**, to synthesize efficient OER and HER nanocatalysts using recycled industrial waste powder, that is a key element for low-impact solutions for energy production.

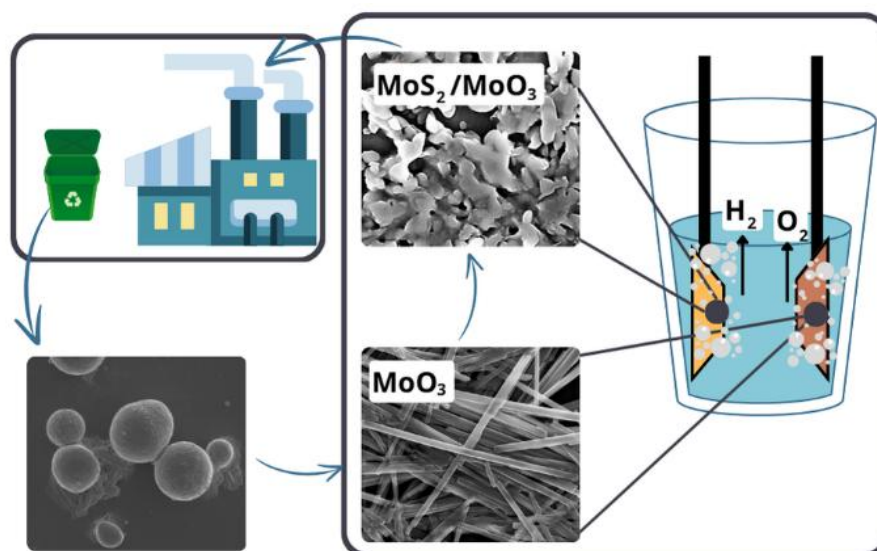


Figure 45 Scheme to synthesize the resulted sustainable project.

Mo-based nanostructures characterised for energy storage applications

Chapter 4. Mo-based nanostructures characterised for energy storage applications

4.1 State of the art on Mo-based nanostructures

As seen in the previous Chapter, MoO₃-nanobelts have promising characteristics and a unique structure, thanks to these features they can also work as supercapacitor, especially in alkaline electrolytes, such as KOH. In fact, many research groups, like Gosh et al., demonstrated a specific capacitance of 136 Fg⁻¹ in a 6M KOH electrolyte in a voltage window from 0 to 1 V [185]. MoO₃ nanobelts were synthesized and characterized by Zhang et al. in a three-electrode electrochemical cell using the standard calomel electrode as a reference, platinum wire as a counter, nickel foam as a substrate for MoO₃ deposited active material, and 3M KOH as the electrolyte. They obtained a specific capacitance of 206 Fg⁻¹ at 1 mV s⁻¹ with a potential range of 0 to 0.65 V [186]. In Section 1.3.1 it was discussed the importance of the ammonium-ion storage, for this reason we decided to study the synthesised MoO₃-nanobelts in an ammonium-based alkaline electrolyte, comparing this performance with the well-studied KOH.

Then, combining the goal to do ammonium-ion storage, with the aim to work with a more environmentally friendly electrolyte, 2D nanostructures based on MoS₂ were studied in ammonium sulphate (hence (NH₄)₂SO₄). These nanostructures captured the attention of many researchers in the last years; indeed, this morphology seems to enhance the electrochemical activity of the material [80]. Usually, 2D-MoS₂ is combined with other materials to obtain heterojunctions which enhance the electrochemical energy storage performances, polymers

Mo-based nanostructures characterised for energy storage applications

and carbon-based materials are often used for this purpose [81], [82]. MoS₂-based electrodes were also studied in different electrolytes, showing how passing from Li⁺ to NH₄⁺ the specific capacitance doubles [62], hence knowledge improvement about the connection between morphology and electrolyte is one of the recent goals in the field [30]. All the cited works use different binders in their mixture, it has important issues like the high environmental impact and the excess covering of the active surface, for these reasons, one of the goals for the future is the absence of addition binders in the material [30].

4.2 MoO₃-nanobelts for energy storage application in alkaline environments

In Chapter 2, the synthesis of orthorhombic MoO₃-nanobelts from Mo-based recycled powder was shown, while in Chapter 3 we study the behaviour of this material for Oxygen Evolution Reaction, seeing promising results respect to state-of-the-art for a pure MoO₃-based electrode. In this section we want to evaluate the energy storage performances of the synthesized nanostructures, without the addition of any materials to improve the conductivity; indeed, the goal is to perform a deeper study on the active mechanisms of the bare material, which can help for future new applications. The electrodes were prepared again as reported in Appendix B.

To evaluate the energy storage performances and mechanism of MoO₃ nanobelts electrochemical analysis were carried out in different electrolytes, 1M KOH and 1M NH₄OH. **Figure 46** reports the CV curves at 100 mVs⁻¹ acquired using the same active material (MoO₃ nanobelts) in 1M KOH and 1M NH₄OH, respectively brown and light green curves. The electrode tested in 1M KOH gives CV curve whose shape is not linked to a specific behaviour, instead the one obtained in

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1M NH_4OH , possesses a shape which is close to that of an ideal pseudocapacitor in these environments with an oxidation peak around -0.2 V [54]. The comparison between the area under the CV curves suggests that the storage of K^+ is favourable with respect to NH_4^+ since a higher area is obtained in case of KOH electrolyte.

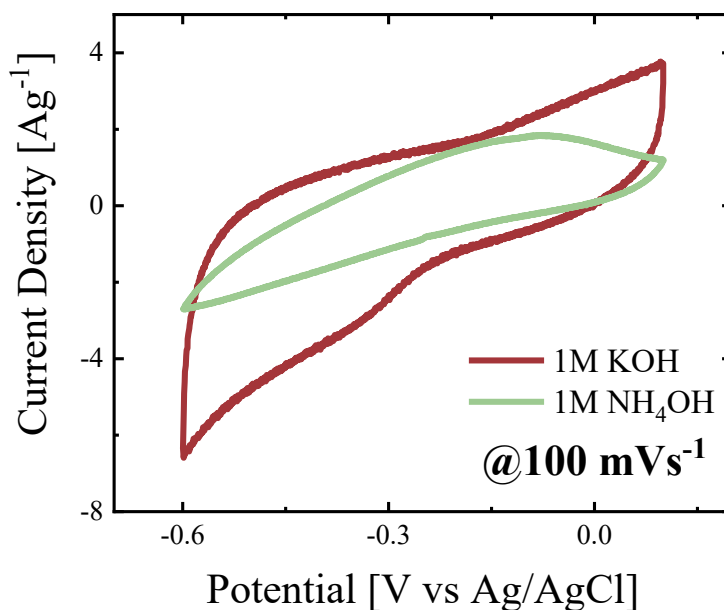


Figure 46 CVs in 1M KOH (brown curve) and 1M NH_4OH (green curve) at 100 mVs^{-1}

Furthermore, to confirm this experimental result, specific capacitance values were extracted from CVs obtained at different scan rates and in both electrolytes (see **Figure 47a** and **Figure 47b**) using Eq.6 (see Appendix A) and they are compared in **Figure 47c**. The MoO_3 nanobelts show higher specific capacitance values in 1M KOH reaching about 290 Fg^{-1} at 5 mVs^{-1} , while a specific capacitance of about 75 Fg^{-1}

Mo-based nanostructures characterised for energy storage applications

¹ is obtained in 1M NH₄OH at the same scan rate. At higher scan rates the specific capacitance values decrease in both cases, this trend can be linked for the dominance of diffusive mechanisms but also to the presence of an electrical resistance for the sample which limits the electrochemical performance.

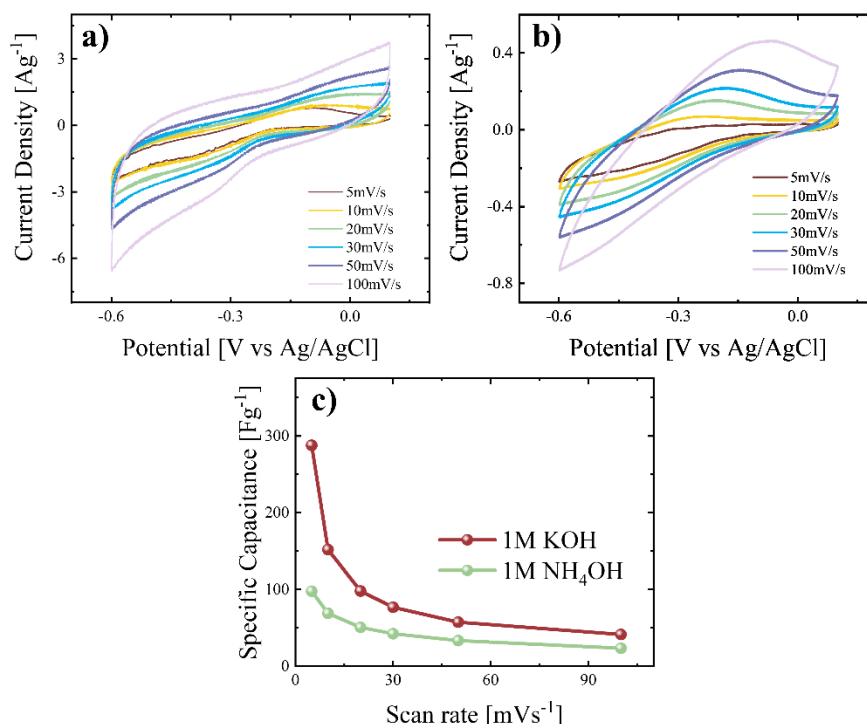


Figure 47 Cyclic Voltammetry (CV) curves at different scan rates in 1M KOH (a) and 1M NH₄OH (b). c) Specific capacitance values extracted from CVs.

Other works reports MoO₃-based electrodes in alkaline electrolytes; a comparison can find in **Table 9**. Comparable potential windows were employed, but a significant improvement of the specific capacitance was registered, and a remarkable improvement for the specific capacitance can be seen. Indeed, the MoO₃-nanobelts synthesised from recycled material show superior specific capacitance in same

Mo-based nanostructures characterised for energy storage applications

electrolyte with lower concentration respect to other works in the literature.

Table 9 Comparison between synthesised material and other MoO₃-based electrodes in alkaline electrolytes.

Electrode material	Electrolyte	Voltage window [V]	Specific capacitance [Fg ⁻¹]	Reference
α -MoO ₃ nanobelts	6M KOH	0 to 1	136	[187]
α -MoO ₃ nanobelts	3M KOH	0 to 0.65	206	[188]
MoO ₃ -MWCNTs	1M NaOH	-0.75 to 0.3	98	[189]
α -MoO ₃ nanobelts	1M KOH	-0.6 to 0.1	290	This work
α -MoO ₃ nanobelts	1M NH ₄ OH	-0.6 to 0.1	100	This work

As seen in the previous table, in the literature several works deal with KOH as electrolyte, hence we decided to perform further analysis to understand the reasons for which K⁺ is favoured for this application. **Figure 48** reports the Galvanostatic Charge-Discharge (GCD) curves at 0.7 Ag⁻¹ acquired for both the electrolytes. The sample tested in 1M KOH shows a shape close to quasi-triangular one, as seen for supercapacitors [190][191][192]. In 1M NH₄OH there is a cusp-like shape, which is characteristic for pseudocapacitors, indeed the change of the slope occurred around -0.2 V is linked to the oxidation reaction at the material surface, also the shape of only discharge curve suggests the presence of intercalation mechanisms with partial redox reactions [193].

Mo-based nanostructures characterised for energy storage applications

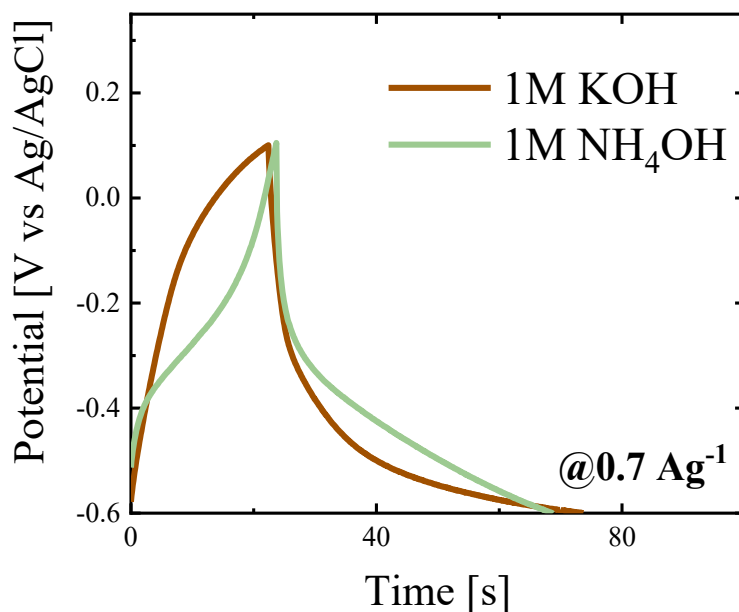


Figure 48 GCD curves of the sample in 1M KOH (brown curve) and 1M NH₄OH (green curve) at 0.7 Ag⁻¹.

The specific capacitance values were evaluated thanks to Eq.12 (see Appendix A) from the GCD curves at different current densities (see **Figure 49a** and **Figure 49b**) and they are in **Figure 49c**, reporting 73 and 58 Fg⁻¹ at 0.7 Ag⁻¹, respectively for 1M KOH and 1M NH₄OH. The sample tested in 1M NH₄OH reports lower values at high current density than the sample tested in the other electrolyte. This behaviour is usually linked to a higher material resistance which limits the storage mechanisms [194].

Mo-based nanostructures characterised for energy storage applications

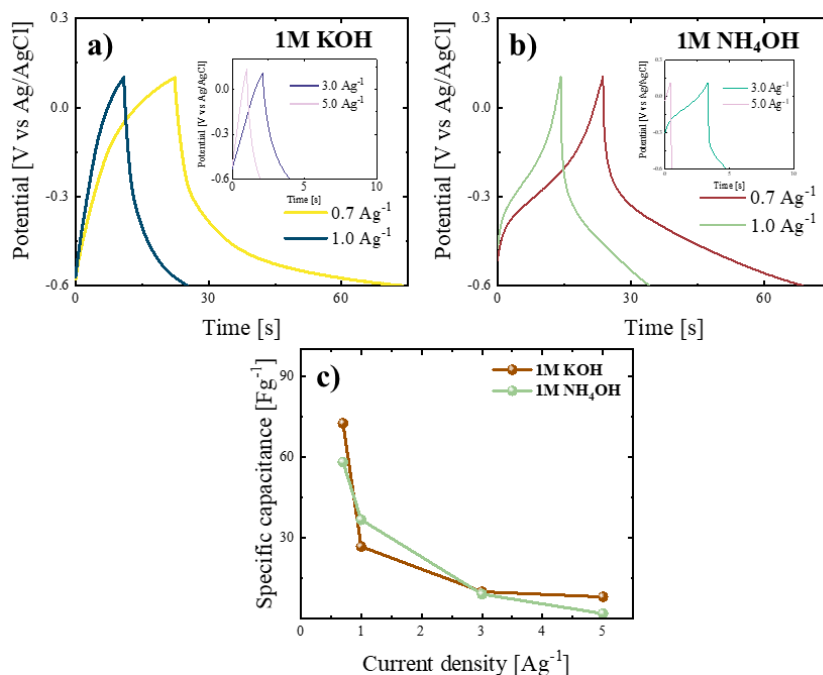


Figure 49 Galvanostatic Charge-Discharge (GCD) measurements for 1M KOH (a) and 1M NH_4OH (b); c) Specific capacitance values calculated from GCD curves.

To validate this hypothesis, iR Drop values were extracted for both electrolytes from GCD curves (see **Figure 50**), using Eq.13 (see Appendix A), inserting the potential difference between end and beginning of charge and discharge curves respectively. As expected, iR drop increases with the current density, but values obtained for the sample tested in 1M NH_4OH are about four times bigger than the ones obtained when sample is tested in 1M KOH. Another important insight is the trend of the iR drop; indeed, it is not linear, suggesting that resistive mechanisms occur which affect the Ohm's law.

Mo-based nanostructures characterised for energy storage applications

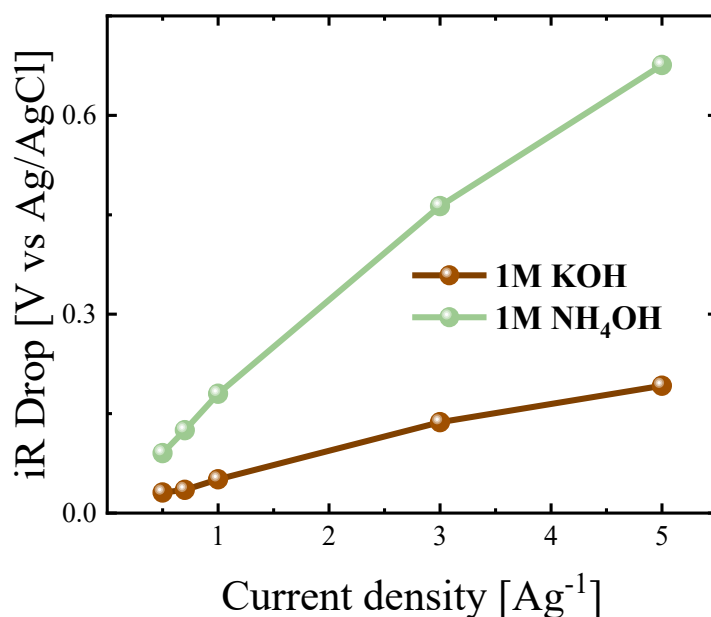


Figure 50 iR Drop values extracted in 1M KOH (brown curve) and 1M NH_4OH (green curve).

To deeply analyse the differences between the electrochemical behaviour in the two electrolytes, EIS measurements were performed at 0 V vs open circuit, to study the electrochemical interaction at the electrode-electrolyte interface. Nyquist plots obtained in 1M KOH and 1M NH_4OH are reported in **Figure 51**, respectively brown and green curves. The uncompensated resistances is an important parameter for electrochemical measurements; it helps to evaluate the electrochemical resistance at the interface electrode-electrolyte which can affects the measurements [195]. It is possible to extract the uncompensated resistance by the Nyquist plot taking the real part of the impedance when the imaginary one goes to zero, in the high-frequencies domain. The extracted uncompensated resistances are equal to 2 and 140 Ω ,

Mo-based nanostructures characterised for energy storage applications

respectively in 1M KOH and 1M NH₄OH. Also, other parameters were evaluated using a fitting based on the Randles circuit, this study is reported in Appendix C.

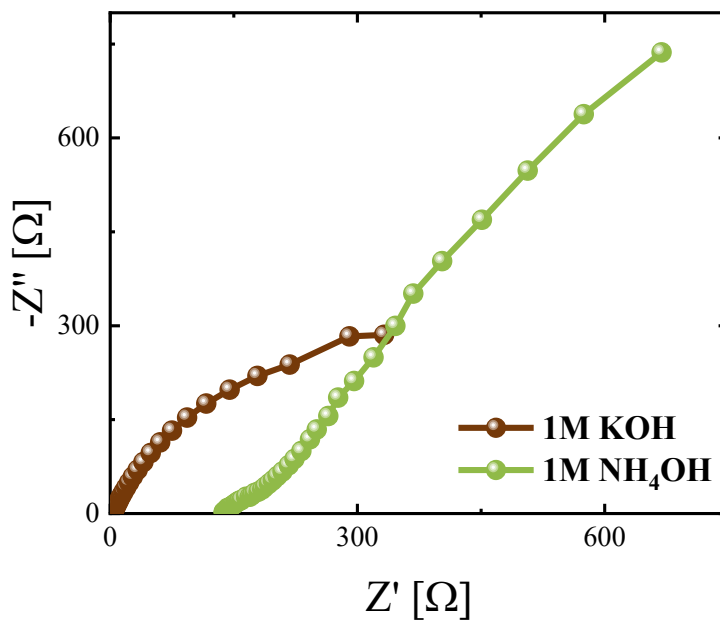


Figure 51 Nyquist plots of MoO₃-nanobelts in 1M KOH (brown curve) and 1M NH₄OH (green curve).

In **Figure 52a** is reported the Magnitude Plot obtained in 1M KOH and 1M NH₄OH, respectively brown and green curves. In both the environments at low frequencies high impedance values can be observed, but the green curve decreases slowly to higher frequencies reaching a plateau close to 100 Ω after 10⁰ Hz, this trend suggests a pseudocapacitive behaviour within this range [196]. Contrary, the brown curve is characterized by a strong decrease of the impedance, that can be linked to a capacitor dominant mechanism, in this case the plateau is for frequencies higher than 10³ Hz and for impedance value

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close to 1Ω [196]. Moreover, the green curve stabilization after 10^0 Hz indicates a resistive-dominant behaviour, while the brown one reaches a stability for frequency higher than 10^3 Hz, hence a capacitive-dominant behaviour for frequencies lower than 10^3 Hz [197]. The sample tested in 1M KOH has a minimum in the Phase Plot (see **Figure 52b**) between 10^0 and 10^1 Hz, which means a capacitor behaviour occurs at these frequencies [197], confirming what seen in the Magnitude plot. The green curve (obtained when sample is tested in 1M NH_4OH) stabilizes close to zero phase very soon respect to the brown one, hence the sample in 1M NH_4OH starts to be resistive before than the one in 1M KOH [197], suggesting a possible link between lower specific capacitance values and resistive behaviour in different hydroxides environments, especially at higher scan rates.

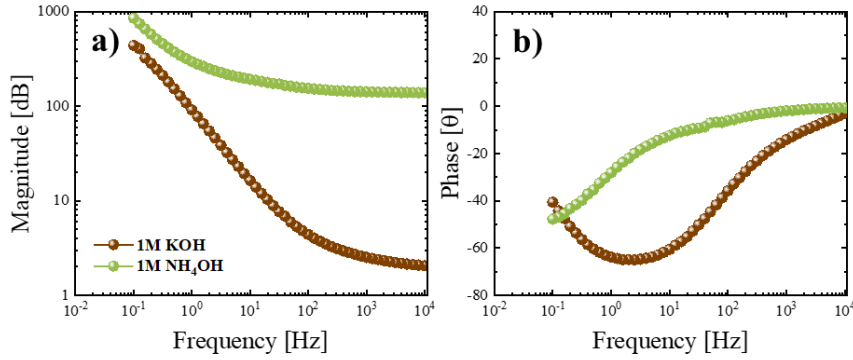


Figure 52 a) Magnitude and b) Phase plots of MoO₃-nanobelts in 1M KOH (brown curve) and 1M NH₄OH (green curve).

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4.3 MoS₂-nanosheets for supercapacitors applications

As previously said, between the goals of this Chapter there are the studying ammonium-ion storage and the development of more sustainable devices. For the second one it is necessary to move to neutral electrolyte, but the synthesised MoO₃-nanobelts are not favourable to work on a neutral environment (see **Figure 53**); while their employment in an ammonium-based electrolyte produces resistive mechanisms in the surface, as seen in the previous section, which ruin the electrochemical performances.

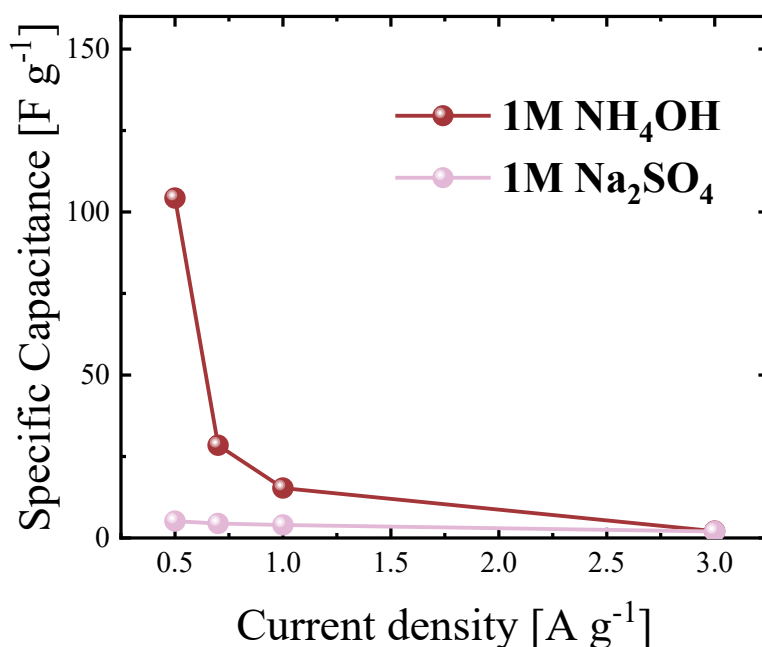


Figure 53 The behaviour of MoO₃-nanobelts in 1M NH₄OH (brown) and 1M Na₂SO₄ (pink).

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MoS₂-nanosheets were widely studied in ammonium-based electrolyte, for this reason we decided to move to this material. In Chapter 2 four different synthetises were shown, seeing the effect of pH and temperature for the morphology and the phase of the material. Here, the different samples will be compared from an electrochemical point of view, eventually observing differences due to the different growth parameters, as previously observed. The electrodes, which were prepared using the inks produced after the four different hydrothermal synthesis (see Appendix B), were studied for electrochemical applications in 1M (NH₄)₂SO₄, which a neutral and environmentally friendly electrolyte. The cyclic voltammograms (CVs) at 100 mVs⁻¹ of the samples are compared (see **Figure 54**). Studying CVs of the samples are characterized by the absence of redox peaks, and they have a rectangular shape, suggesting that non-Faradic processes dominate as a storage mechanism [54]. The CV curves seem to be symmetrical to zero, suggesting a good reversibility for the sample [30].

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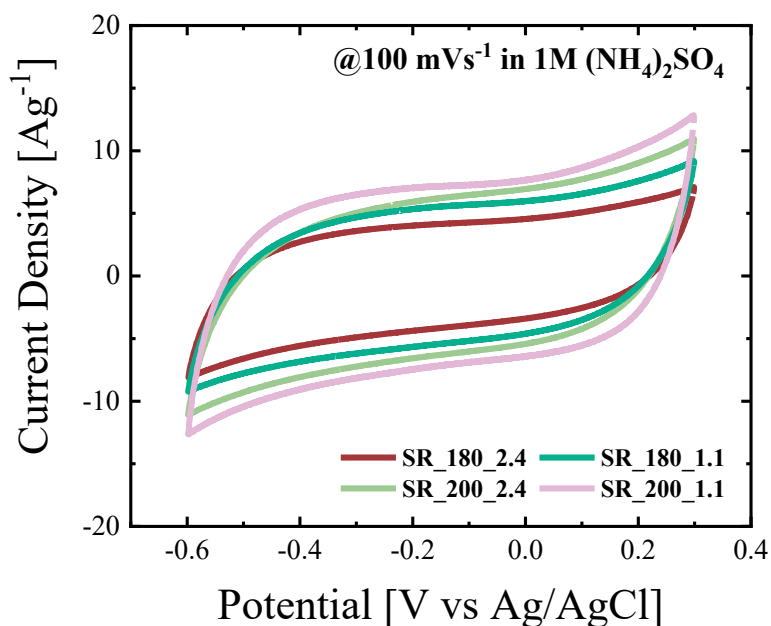


Figure 54 CVs at 100 mVs⁻¹ of the different MoS₂-based samples.

The described behaviour is shown also at different scan rates for all the samples, as reported in **Figure 55**. A quasi-rectangular shape can be observed for all the sample, from SR_180_2.4 to SR_180_1.1 the current densities values increase, but the real jump to superior performances can be observed with the samples synthetized at 200 °C, here the area is larger. Finally, SR_200_1.1, obtained modifying both pH and temperature, shows the maximum values for the current densities, preserving the quasi-rectangular shape.

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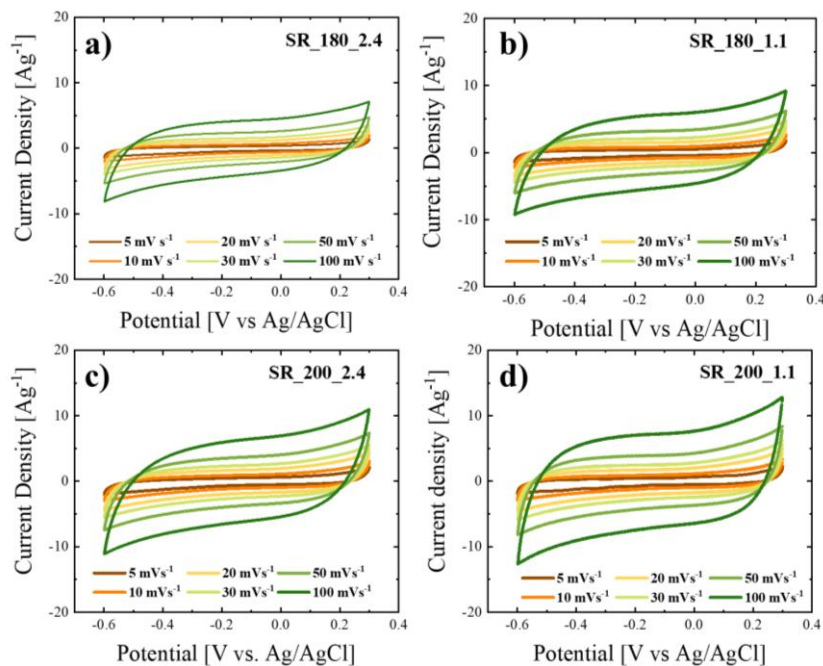


Figure 55 CV curves at different scan rates for the samples a) SR_180_2.4, b) SR_180_1.1, c) SR_200_2.4 and d) SR_200_1.1 in 1M (NH₄)₂SO₄.

These CV curves at different scan rates are employed to evaluate the specific capacitance values for each sample using Eq.6 (see Appendix A), the values are reported as a function of scan rate in **Figure 56**. High values were recorded at a low scan rate, about 200 Fg⁻¹ at 5 mV s⁻¹ for the synthesis SR_180_2.4, which is just a promising result for bare MoS₂ in neutral electrolyte; but increasing the synthesis temperature, we obtained about 400 Fg⁻¹ for the samples SR_200_2.4 and SR_200_1.1. The control of the pH seems to have an effect at higher scan rates, indeed SR_200_1.1 has a specific capacitance of 143 Fg⁻¹ against 123 Fg⁻¹ of SR_200_2.4. As suggested by the CV curves shape, all the samples have a capacitive behaviour, but the one with thinner average size for the nanostructures has a better behaviour at higher scan rates.

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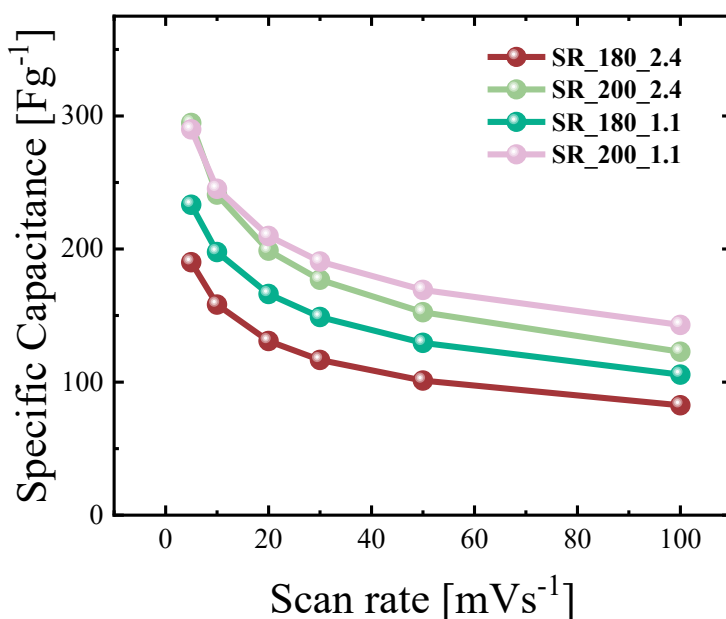


Figure 56 The specific capacitance values for the synthesis at different scan rates.

Further, to study the nature of the active mechanisms, Dunn's model was employed to evaluate in detail surface-capacitive and ion-limited diffusion contributions for the storage, since, following this model, the measured current can be described Eq.8 (see Appendix A). Hence, we are able to evaluate the surface capacitive content at the current measured during energy storage at different scan rates. **Figure 57** reports the surface capacitive percentage for each material at lower scan rates. The analysis was conducted at -0.15 V vs Ag/AgCl. All the samples show a dominance of surface capacitive mechanisms, enforcing the idea that we are working with supercapacitors [198]. Comparing the samples with each other, SR_200_1.1 shows the highest surface capacitive percentage, which can help to obtain a material with better reversibility. This result can be linked to the morphology of the

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sample, due to the MoS₂-nanosheets, which is a thinner structure than previous samples, these synthesised materials have a superior exposed surface, in accordance with the capacitive behaviour observed thanks to the CV curves shape and the Dunn's model results.

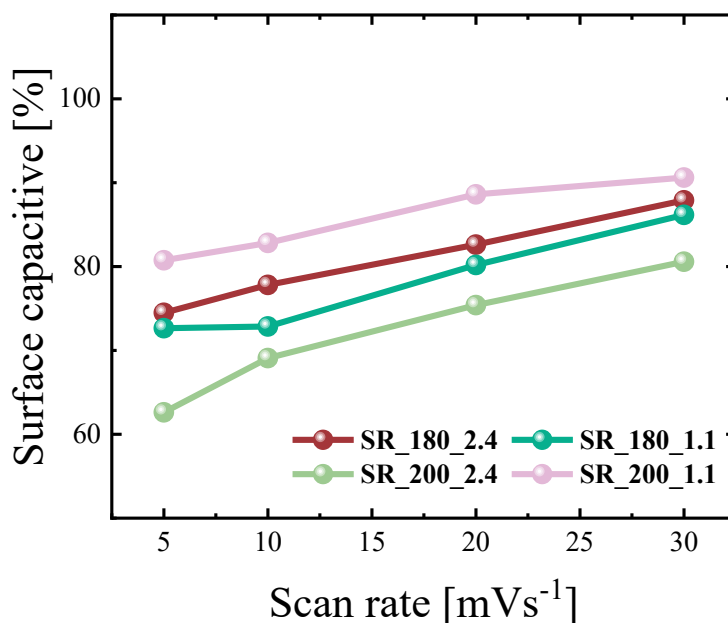


Figure 57 Dunn's model was used to analyse the active mechanism.

An estimation of the effective surface area was done employing Eq.9 (see Appendix A) to evaluate the Electrochemical Surface Area (ECSA). In this formula, C_s is theoretical specific capacitance, which is calculated for a planar electrode in an aqueous electrolyte, and equal to $40 \mu\text{Fcm}^{-2}$ [199]; while C_{dl} , which is the electrochemical double-layer capacitance, is extracted from CVs using the current density values for each scan rate at a fixed potential, and it can be obtained using Eq.10 (see Appendix A). As suggested by Eq.10, the collected current density values at $-0.15 \text{ V vs Ag/AgCl}$ were plotted as a function of the scan rate,

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the extracted slope is the electrochemical double-layer capacitance (C_{dl}), which was evaluated to calculate the ECSA of the material (see **Figure 58**) and to validate what we seen with the Dunn's model.

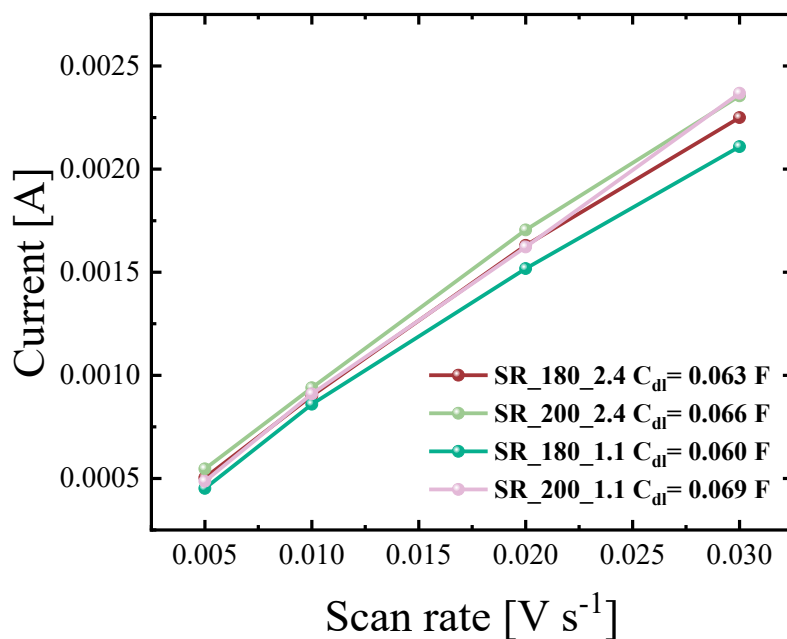


Figure 58 Evaluation of electrochemical double-layer capacitance for each sample at low different scan rates.

The slope of the linear fit corresponds to C_{dl} , and it is used to calculate the ECSA value using Eq.9, the results are reported in **Table 10**.

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Table 10 ECSA values evaluated from the curves in Figure 58.

Sample	ECSA [10^3 cm^2]
SR_180_2.4	1.59 ± 0.07
SR_200_2.4	1.65 ± 0.07
SR_180_1.1	1.51 ± 0.05
SR_200_1.1	1.74 ± 0.05

The calculated values are also reported in **Figure 59** to highlight how the combined action of temperature and controlling pH of the solution before the hydrothermal treatment allows an increase in the ECSA, together with a decreasing of the nanostructures size, confirming what seen with the previous analysis.

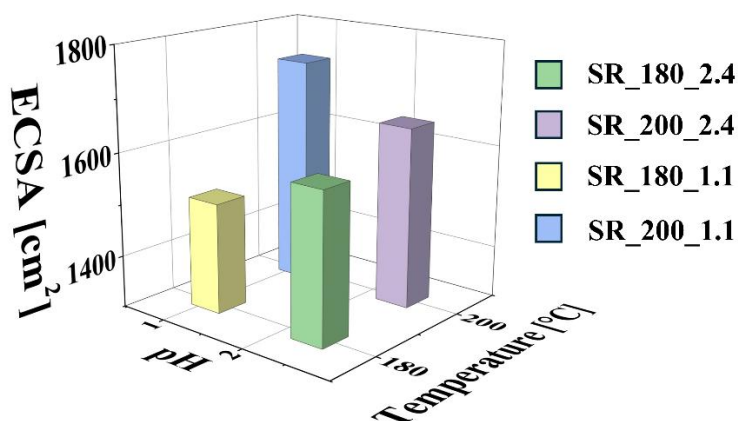


Figure 59 ECSA values calculated for each sample.

The different samples were also compared in **Figure 60** with the GCD curves recorded at 0.5 Ag^{-1} , they present quasi-triangular shapes, confirming the idea of fast kinetics linked to our sample and the

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combination of capacitive and pseudocapacitive mechanisms to enhance both energy and power density of the materials. The samples produced at 200 °C shown superior performances respect to others, among these the best one seems to be the sample synthetized controlling the pH thorough HCl addition, with a larger discharge time.

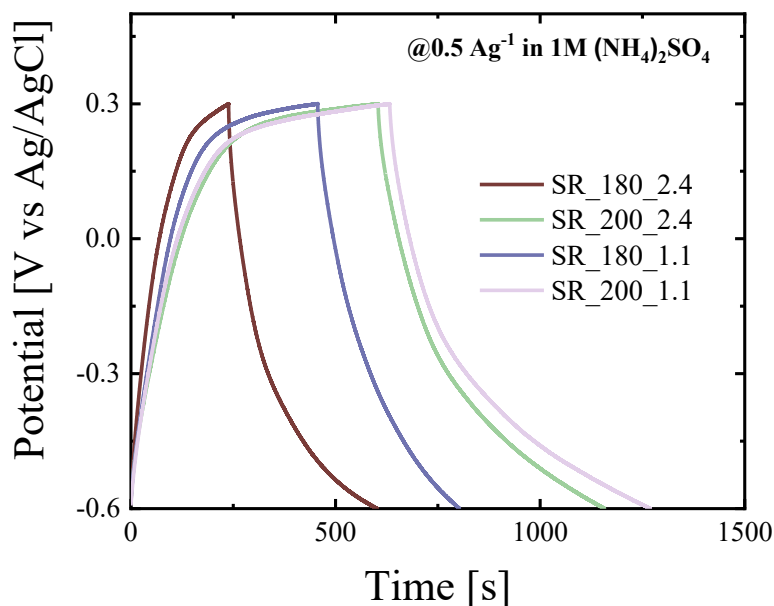


Figure 60 GCD measurements were performed for all the samples, and the ones at 0.5 Ag^{-1} were used to do a comparison

The samples shown a similar behaviour also at different current densities, which are reported in **Figure 61**. The sample SR_200_1.1 shows superior performance also at higher current densities respect to others. For all the samples at higher current densities can be seen a quasi-triangular shape, which can be linked to a supercapacitor behaviour.

Mo-based nanostructures characterised for energy storage applications

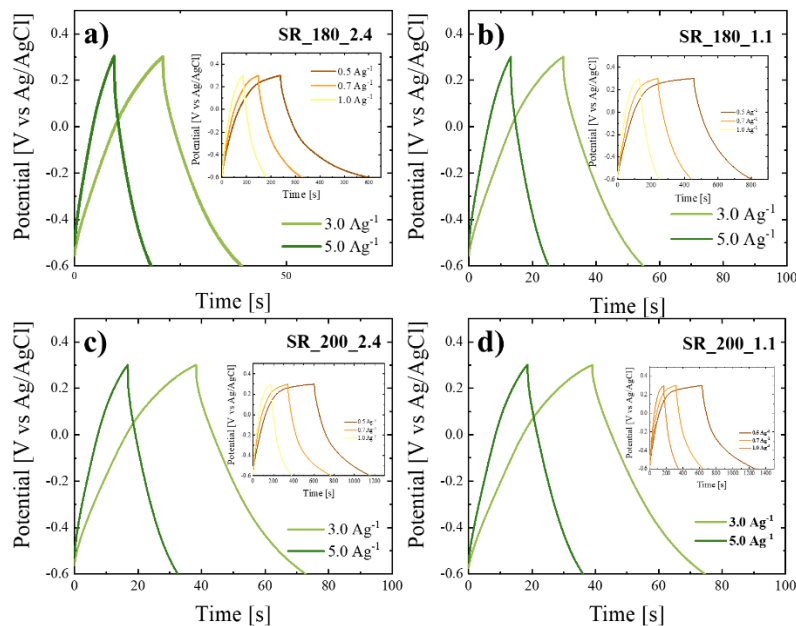


Figure 61 GCD curves at different current density for the synthesis a) SR_180_2.4, b) SR_180_1.1, c) SR_200_2.4 and d) SR_200_1.1, the measurements were done in 1M $(\text{NH}_4)_2\text{SO}_4$.

For a better comparison we analysed the previous curves to extract different information. Firstly, we evaluated the specific capacitance values (see **Figure 62**) obtained putting in Eq.12 (see Appendix A) the discharge times that we can extract from GCD curves, about 150 Fg^{-1} was evaluated at 0.5 Ag^{-1} for the samples synthetized at 180°C . It is a promising result for only MoS_2 with respect to other works, where it is possible to find 100 Fg^{-1} for MoS_2 sample [62]. But the materials obtained at 200°C recorded 200 Fg^{-1} at 0.5 Ag^{-1} , and between these two, the one synthetized controlling the pH also showed an interesting behaviour at higher current densities, about 90 Fg^{-1} at 5 Ag^{-1} .

Mo-based nanostructures characterised for energy storage applications

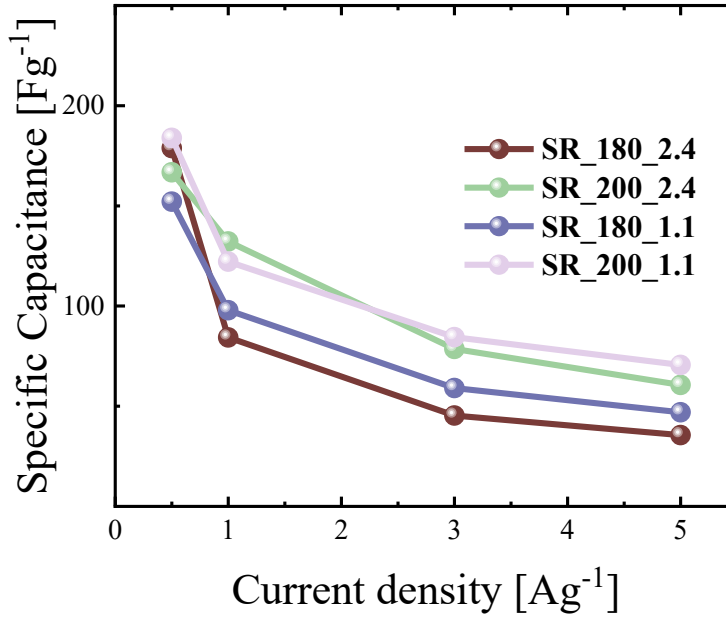


Figure 62 GCD measurements of the samples evaluated at different current densities.

The sample SR_200_1.1 was also compared with the literature, finding that it doubles other works concerned with MoS_2 -based electrodes [62].

The GCD curves were also used to evaluate material iR drop (see **Figure 63**) at different current densities, they were calculated using Eq.13 (see Appendix A), it allows to evaluate the efficiency of the ohmic contact, hence of the sample. The values increase up to 0.125 V at 5 Ag^{-1} for the sample SR_180_2.4, which is comparable to other works [56]. While other samples registered lower iR drop values, in particular the synthesis SR_200_1.1 shows an iR drop 2.1 times lower than SR_180_2.4 starting sample, it is quite lower also than other works in the literature [62]. The sample with the superior exposed surface area has the lower iR drop, suggesting that the superior behaviour at higher scan rates and energy densities is linked to the decreased size of the

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nanostructures due to the manipulation of the growth parameters. Finally, it is possible to notice the linearity of the iR drop respect to the current densities for all the samples, this means that the Ohm's law is valid also at higher current densities.

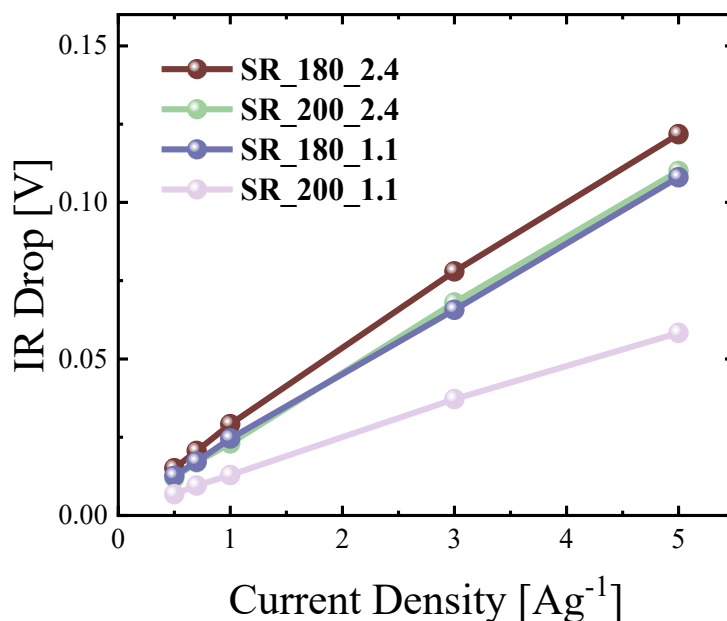


Figure 63 iR Drop values were evaluated for each sample at different current densities.

Figure 64 shows the Electrochemical Impedance Spectroscopy (EIS, Appendix A) of the samples at the open circuit; these curves allow to study the electrode-electrolyte interface through the response of the material at potential perturbations. The contact resistances (R_u) at the interface with the electrolyte were directly determined by seeing the x-intercept of EIS plot, and it is equal to 2.62Ω for SR_180_2.4, while for SR_200_1.1 a resistance of about 2.1Ω was registered. These values are lower than other works in the literature [62]; this behaviour can be linked to the nanosheets' morphology, which allows access to a great

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surface area active for adsorption, and the lower R_u SR_200_1.1 can be linked to the higher ECSA calculated for that sample, explain also the lower iR Drop at higher current densities, and the better behaviour of the sample at superior scan rates.

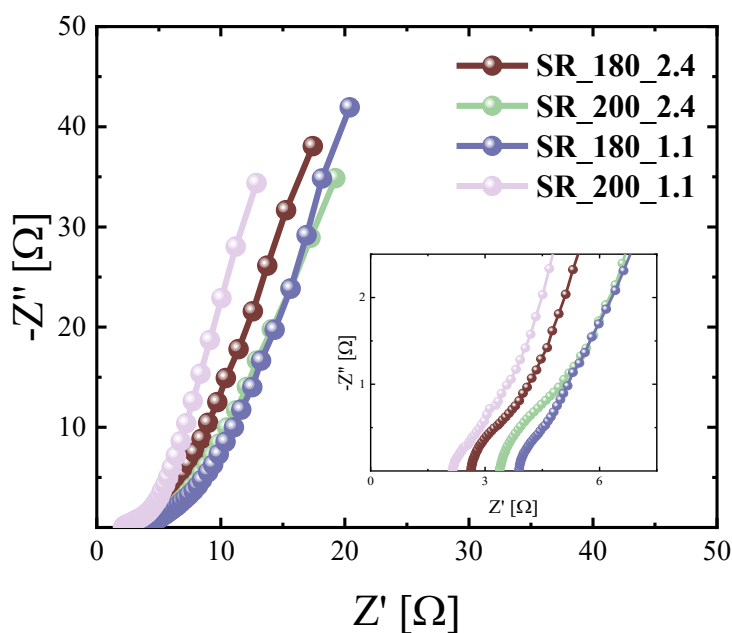


Figure 64 EIS data were also taken for each sample.

4.4 Conclusions

In this Chapter different insights came out, firstly the electrochemical performances of the α -MoO₃ were studied in two different hydroxide environments, 1M KOH and 1M NH₄OH, showing another application respect to the previous Chapter. The CV curves shape was analysed, showing a pseudocapacitor behaviour for the material in 1M NH₄OH, while α -MoO₃ nanobelts show a supercapacitor behaviour in 1M KOH. The sample reaches about 300 and 100 Fg⁻¹ at 5 mVs⁻¹, respectively in

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1M KOH and 1M NH₄OH. The different behaviour for the material in the two environments was also investigated using GCD curves. The cups-like shape obtained in 1M NH₄OH confirms that the sample acts as a pseudocapacitor, while in 1M KOH it works as a supercapacitor. The specific capacitance extracted by the curves is about 50 Fg⁻¹ for both electrodes, suggesting that the electrochemical performances were limited by the electrochemical resistance at the electrode-electrolyte interface. Furthermore, EIS measurements were recorded to study the electrochemical processes, revealing high resistance values for both the environments. However, Magnitude and Phase plots suggested that in 1M NH₄OH there is a superior resistance behaviour than 1M KOH for the material. The results suggest that potassium ions are favoured for the storage in MoO₃-nanobelts; indeed, ammonium ones encounter different resistive mechanisms as also suggested by what extracted from EIS data.

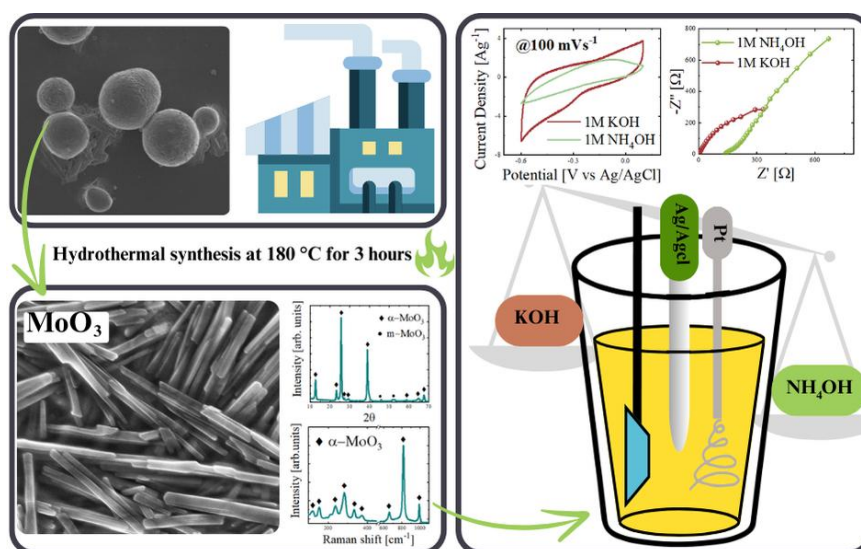


Figure 65 Resume of MoO₃ for energy storage application.

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Also, MoS₂-nanosheets were studied with interesting results, indeed CVs show supercapacitors' behaviour, due to the quasi-rectangular shape, with promising results for the synthesis SR_200_1.1 with a specific capacitance of about 300 Fg⁻¹. Dunn's model to evaluate the percentage of surface-active mechanisms, finding that the combination of temperature and pH improves it. This result is linked to the ECSA trend, which shows that the sample SR_200_1.1 has the highest ESCA value. GCDs show the hybrid behaviour of supercapacitors; indeed, capacitive and pseudocapacitive behaviours are observed. Again, the best performances were obtained for the sample SR_200_1.1, with a specific capacitance of about 200 Fg⁻¹. But it is also the sample with the lowest iR Drop, suggesting a lower energy loss. While EIS measurements showed a lower contact resistance managing both the growth parameters, hence for SR_200_1.1.

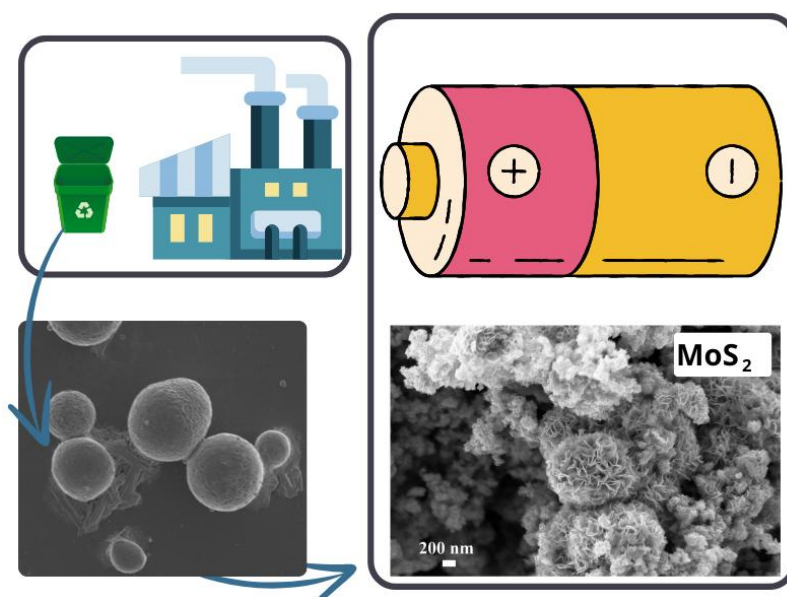


Figure 66 Schematization of MoS₂-nanosheets for energy storage application.

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Seeing MoO_3 -nanobelts and MoS_2 -nanosheets iR drop trends it is possible to highlight the different active mechanisms. For MoO_3 -nanobelts the non-linearity of the sample in different electrolyte show that the Ohm's law does not work, probably due to resistive mechanisms which occur, and CV and GCD curves confirm this suggestion. On the other hand, different insights show the supercapacitor behaviour of MoS_2 -nanosheets, which report a linear iR drop, hence the Ohm's law is working. The electrochemical activity of MoS_2 -nanosheets demonstrated to be influenced by the temperature of the hydrothermal process. The increasing of only 20°C produced important differences, as seen from the shown specific capacitance and ECSA values. The temperature effect was also combined with the variation of the pH, in Section 2.4 thanks to this modification thinner nanostructures were produced, where the edge sites work like active one, as suggested by the ECSA value of SR_200_1.1 that is higher than SR_180_1.1 one.

Coin cell based on MoS₂-nanosheets: a device for technological transfer

Chapter 5. Coin cell based on MoS₂-nanosheets: a device for technological transfer

5.1 Knowledge should not remain in a desk: Technological Transfer

According to Cambridge's dictionary, the word "technology" stands for "knowledge, equipment, and methods that are used in science and industry"[200], which suggests a link between research and productive worlds. In this context, the importance of innovation as an engine for economic and social development is well-known and studied since the last century, as proven by the works of Schumpeter [201]. Another clarification is needed, indeed, with the world innovation we include new combinations of equipment and ideas which just exist, or new ones; in general, innovation is something able to open unexplored routes - social, economic or political- through the implementation of something new [202]. But to produce an impact on our life innovation and knowledge produced in a lab need to move to industry, and here we start to talk about "Technology Transfer", the definition of this practise can vary as a function of the research field, but in general it stands for the movement of know-how, ideas, proof-of-concept and technological knowledge from one organizational setting to another [203].

To better understand the different processes and moments which occur when a technology is under development, it is possible to employ the "Technology Readiness Levels" (TRLs) metric [204], [205]. According to this system of measurement a distinction can be done, usually the research done in the University starts from TRL 1 and reach TRL 3 [206], then, from 4 to 6 there are institute of research which promote

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the multidisciplinary, helping an improvement of the technology [202], while for superior TRL levels the industry is involved.

The results obtained in the previous Chapter correspond to TRL 3, indeed, the tests in 3-electrode setups are a proof-of-concept for the development of a new and efficient material for energy storage applications. Also, a deeper understanding of the working mechanisms was done, but it was not enough to be competitive with cutting-edge works in the literature.

In this Chapter, firstly it is shown an optimization of the electrode again in a 3-electrode setup, with the goal to enhance the electrochemical performance. Once reached this aim, an increase of the TRL is evaluated through the implementation of the studied electrode in a coin cell device, which is a two-electrode one, with an environment closer to a daily one. Building a working-prototype based on the synthesized MoS₂-based material new insights about the material will be available.

A deeper understanding of the mechanisms is also studying object of this Chapter, for this reason no binder and carbon-based materials will be added to improve the performance of the MoS₂-based electrode. Here a comprehension of the behaviour of the bare MoS₂ want to be performed in a relevant setup, to understand possible bottlenecks.

5.2 Effect of the substrate

An important step to enhance the electrochemical performance of the synthesised material is the proper choice of a substrate. As seen in different works in the literature, the role of the substrate to deposit the synthesised nanostructures is crucial to enhance the material performance [30]. This can be explained by seeing how the interaction nanostructure-substrate affects the electrochemical performances [207]. For this reason, we decided to switch from Graphene Paper to Carbon Paper, which presents a superior porosity with respect to the previous

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one. The bare substrate was tested in the same electrochemical conditions as the MoS₂-based samples, hence in a 3-electrode setup in a potential window between -0.6 and 0.3 V vs Ag/AgCl in 1M (NH₄)₂SO₄ (see **Figure 67**). No capacitive behaviour can be seen for the bare Carbon paper in the same electrochemical conditions used for the MoS₂-based sample.

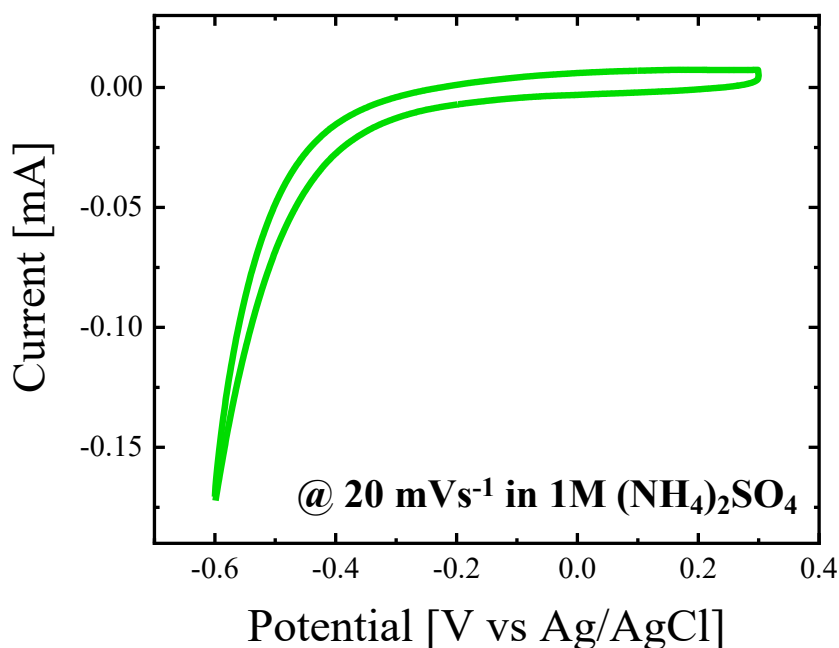


Figure 67 A CV scan on the bare electrode substrate was performed, between -0.6 and 0.3 V vs Ag/AgCl at 20 mV s⁻¹ in 1M (NH₄)₂SO₄.

Then, we drop-casted sample SR_200_2.4 analysed in the previous Chapter on the new substrates, and we tested it in the same electrochemical conditions. Again, in 1M (NH₄)₂SO₄, with a catalyst loading of about 1.2 mg cm⁻². We labelled the sample with the material

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deposited on Graphene Paper as GP+SR_200_2.4, while the one with Carbon Paper as CP+SR_200_2.4. The CVs recorded at different scan rates for GP+SR_200_2.4 and CP+SR_200_2.4 are shown in **Figure 68a** and **Figure 68b**, respectively. Varying the substrate, the CVs acquire an elongated shape closer to the edge of the potential range, while for GP+SR_200_2.4 there is a clear rectangular shape, for CP+SR_200_2.4 it is possible to talk of a leaf shape. This shape suggests a dominance of diffusive capacity, hence a pseudocapacitance behaviour for the few-layered MoS₂ [208]. This variation in the behaviour can be linked to the different porosity of the substrates; indeed, the disposition of MoS₂-nanostructures on Carbon Paper favours the diffusion of ions on the bulk of the overall electrode.

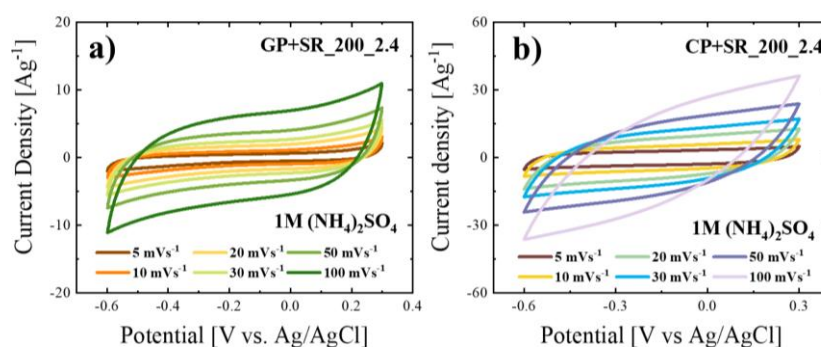


Figure 68 CVs at different scan rates for the material deposited on a) Graphene Paper and b) Carbon Paper.

In **Figure 69a** the comparison of the CVs recorded at 100 mVs⁻¹ is shown, and it highlights the discussed differences for the shapes, but also the current density increases, varying the substrate. Considering that the catalyst loading is the same for the two samples, the different disposition affects the electrochemical performance. This fact it is also confirmed by the specific capacitance values (see **Figure 69b**) calculated using Eq.6 (see Appendix A), here, the sample

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CP+SR_200_2.4 reports values about four times higher than GP+SR_200_2.4.

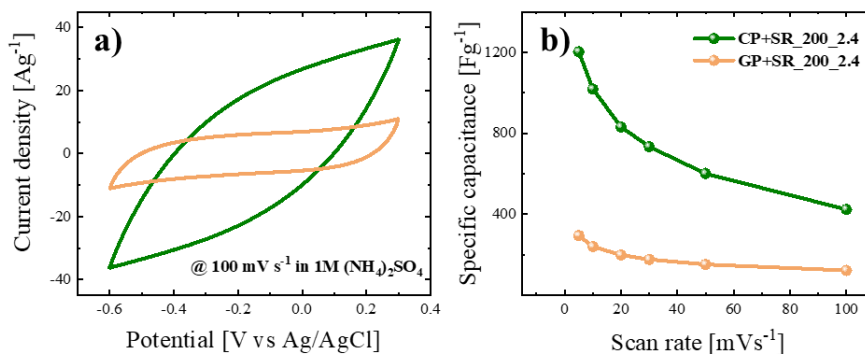


Figure 69 Comparison between a) CVs at 100 mV s⁻¹ for the two sample and b) Specific capacitance evaluated at different scan rates.

Further analyses were performed on the CV curves to study the different behaviours. Eq.7 (see Appendix A) was employed to do Power Law calculations, the results are reported in **Figure 70a**, finding 0.77 and 0.79 for CP+SR_200_2.4 and GP+SR_200_2.4, respectively. The previous analysis did not give clear insights into the different mechanisms in the samples [56]. For this reason, we employed the Eq.8 (see Appendix A) to apply the Dunn's model, the results are shown in **Figure 70b**, here a different behaviour can be seen, indeed GP+SR_200_2.4 reports a superior percentage of surface capacitive mechanism than CP+SR_200_2.4, confirming that in the last sample diffusion processes are more dominant than the previous one [93], [209].

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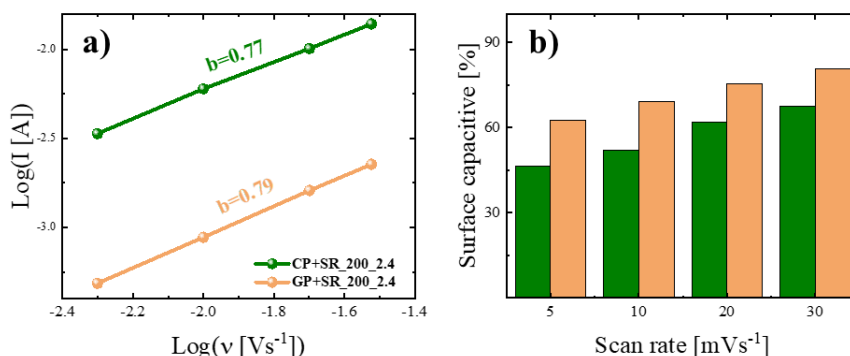


Figure 70 a) Power Law and b) Dunn's method applied on the samples.

Eq.10 (see Appendix A) was employed to calculate the double-layer capacitance (C_{dl}) from CV curves. It is the calculated slope when we plot (see **Figure 71**) the average current as a function of the scan rate for low ones [210]. CP+SR_200_2.4 shows 7 times higher C_{dl} than GP+SR_200_2.4. The calculated C_{dl} values were used to evaluate the Electrochemical Surface Area, using Eq.9 (see Appendix A), where C_s is the theoretical specific capacitance for a planar electrode in an aqueous electrolyte (equal to $40 \mu\text{Fcm}^{-2}$ [199]). We found an ECSA of about 10635.5 cm^2 for CP+SR_200_2.4, against 1648 cm^2 for GP+SR_200_2.4. Hence, a superior electrochemically active area is present for CP+SR_200_2.4 sample, this result can be linked to the pseudocapacitor behaviour shown by it [211], with respect to GP+SR_200_2.4.

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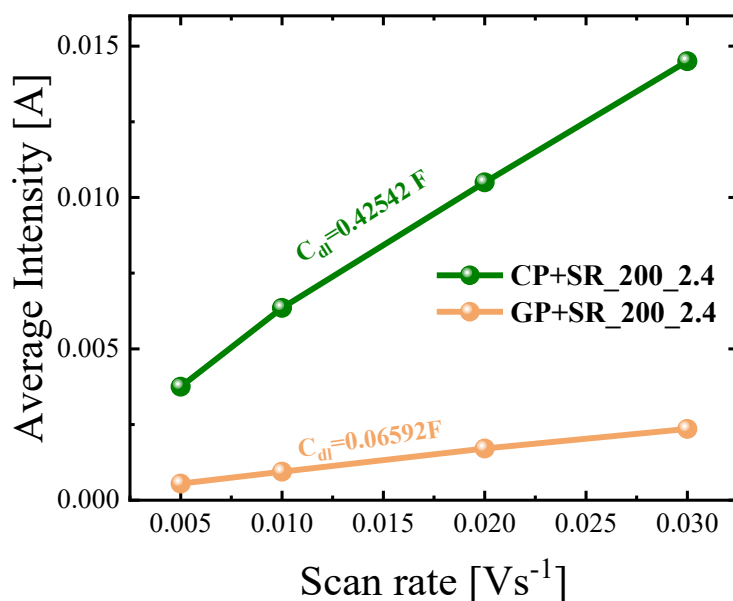


Figure 71 The C_{dl} was calculated for both the samples in order to evaluate their ECSA.

To further study the effect of the substrate we also performed GCD measurements at 3 and 5 Ag⁻¹ (see **Figure 72a** and **Figure 72b**), using the same electrochemical setup previously employed. In both the sample, a quasi-triangular shape can be seen, but for the sample CP+SR_200_2.4, a higher discharge time than the other can be seen.

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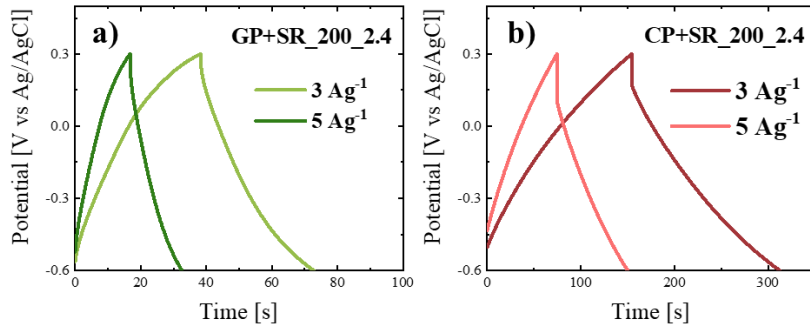


Figure 72 The GCD curves at 3 and 5 Ag⁻¹ are shown for a) GP+SR_200_2.4 and b) CP+SR_200_2.4 in 1M (NH₄)₂SO₄.

From the GCD curves, the specific capacitance values were obtained using Eq.11(see Appendix A) and reported in **Figure 73a**. Here, it is possible to observe a specific capacitance value about 4.7 times superior for the sample CP+SR_200_2.4 than GP+SR_200_2.4. Parallely, we evaluated the iR drop using the Eq.13 (see Appendix A), which is higher for sample CP+SR_200_2.4, this result can be linked to the pseudocapacitance behaviour which increases the global resistance of the sample, hence the energy loss, because to the pseudocapacitance behaviour is associated with a higher charge transfer resistance, which is not in EDLC [212].

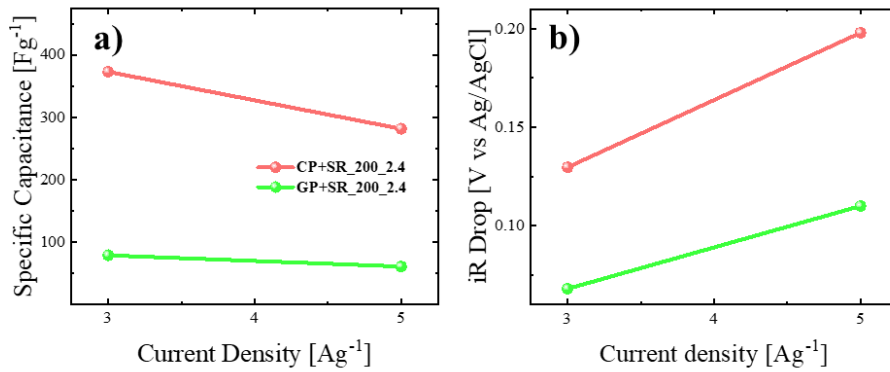


Figure 73 a) Specific capacitance and b) iR Drop evaluated from GCD curves.

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These results were compared with the state-of-the-art in **Table 11**, showing a promising electrode at high current density respect to other works, especially for the absence of any kind of binders.

Table 11 Here the sample are compared with others MoS₂-based electrodes in 1M (NH₄)₂SO₄

Sample	Current density [Ag ⁻¹]	Specific capacitance [Fg ⁻¹]	Reference
2H-MoS ₂	5	60	[62]
MoS ₂	5	125	[213]
MoS ₂ @AlOOH	5	200	[213]
MoS ₂	4	250	[214]
CP+SR_200_2.4	5	280	This work

EIS analysis was performed on the samples to further study the behaviour at the interface. **Figure 74** reports both the points collected, varying the frequency. The uncompensated resistance (R_u) can be evaluated by studying the x-intercept in the high frequency region, 3.45 Ω and 4.42 Ω were obtained for GP+SR_200_2.4 and CP+SR_200_2.4, respectively. Confirming what seen by analysing the iR drop, hence a superior resistance for CP+SR_200_2.4. This sample also shows two straight-line regions, suggesting two different diffusive mechanisms which occur, one of which goes to superior impedance values in the low frequency region, in accordance with a pseudocapacitor behaviour [212], [215].

Coin cell based on MoS₂-nanosheets: a device for technological transfer

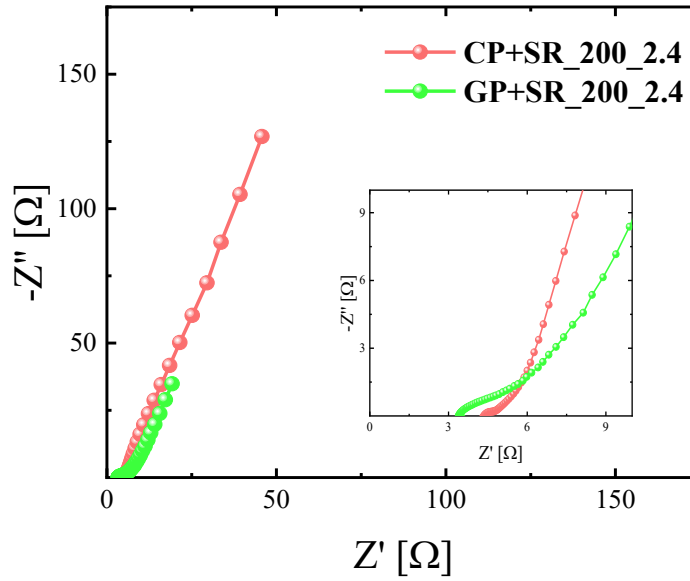


Figure 74 EIS profiles of the material on different substrates.

5.3 Coin cells devices with commercial activated carbon

Once the sample was characterised with the new substrate, it was transferred to a coin cell device, with a 2-electrode one, as schematized in **Figure 75**. The case of CR2032 coin cell was employed to assemble this proof-of-concept device. The device can be divided into different layers. First, we have the two cases, within which the electrodes are displaced. A spacer is added to maintain a fixed pressure between the electrodes. This pressure allows the electrodes to remain constantly in contact with the glass fibre membrane inserted between them, which was wetted with aqueous electrolyte (1M (NH₄)₂SO₄), and it has a diameter of 18 mm. “Electrode +” stands for the working electrode

Coin cell based on MoS₂-nanosheets: a device for technological transfer

(WE), which in this case is the MoS₂-based material studied in the previous section. In literature, different possibilities were evaluated for the “Electrode -” which work as counter and reference electrode (CE and RE, respectively). As a first attempt, we decided to produce an electrode based on activated commercial porous carbon, with Carbon Paper as substrate.

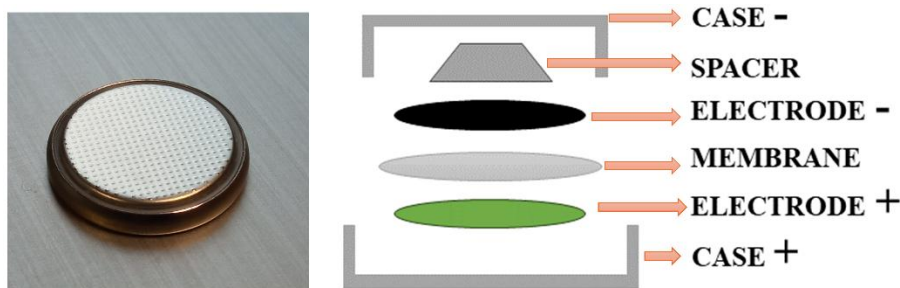


Figure 75 Cross section of the coin cell device based on a CR2032 case; here the disposition of the different layers is reported, with glass fibre membrane between the electrodes and the spacer to keep them under pressure.

In a 2-electrode setup, a charge balance is crucial for the system; hence, before assembling the coin cell a characterisation in a 3-electrode setup was done (see **Figure 76**), a specific capacitance of 14 Fg^{-1} was evaluated for an electrode of 3 mg cm^{-2} . The calculated specific capacitance was inserted into Eq.14 (see Appendix A) to evaluate the needed mass of porous carbon to compensate for the charge in the coin cell system with the MoS₂-based electrode as WE. To assemble the coin cell, the porous carbon was deposited on an aluminum substrate using N-methylpyrrolidone (NMP) and polyvinylidene fluoride (PVDF) to create a slurry (see Appendix B), which was deposited on a substrate of aluminium foil, then it was dried overnight within an oven at 60°C .

Coin cell based on MoS₂-nanosheets: a device for technological transfer

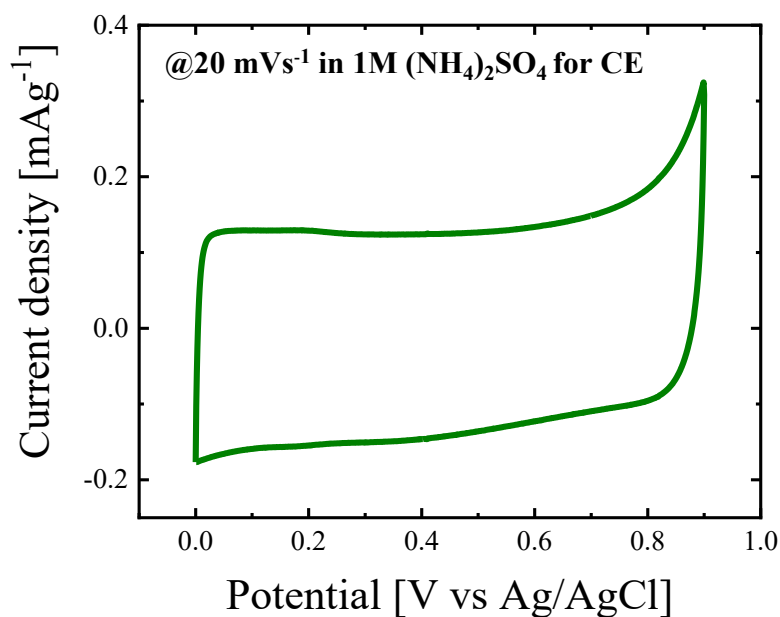


Figure 76 CV measured for the porous carbon electrode.

The assembled coin cell was filled with about 100 μL of 1M $(\text{NH}_4)_2\text{SO}_4$, then the electrochemical measurements were performed by connecting it to a potentiostat. First, CVs at different scan rates were recorded and reported in **Figure 77a**, a leaf shape can be seen for the device, which we can link to a pseudocapacitor behaviour [211], as just seen in the 3-electrode setup. Thanks to Eq.6 (see Appendix A) was employed to evaluate the specific capacitance from the CVs, reaching 165 Fg^{-1} at 5 mVs^{-1} , decreasing to 75 Fg^{-1} at 100 mVs^{-1} .

Coin cell based on MoS₂-nanosheets: a device for technological transfer

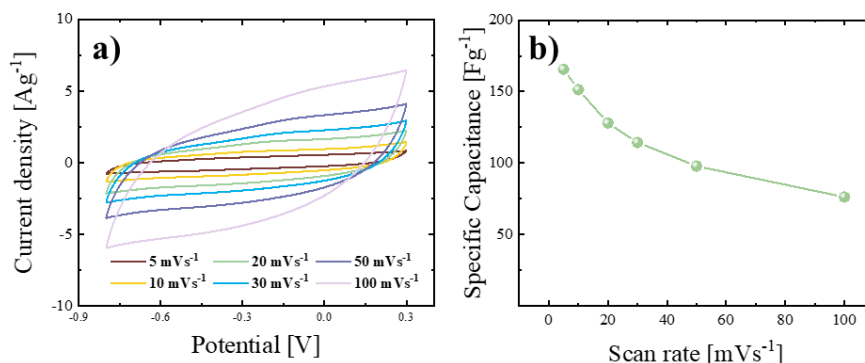


Figure 77 a) CVs at different scan rates were recorded for the asymmetric coin cell based on porous carbon; b) specific capacitance values were evaluated for each scan rates.

Further studies were conducted using GCD curves (see **Figure 78a**). Firstly, we employed them to analyse the behaviour of the sample; indeed, a quasi-triangular shape can be observed, which suggests a supercapacitor trend for the material. GCD curves were also used to evaluate the specific capacitance values of the material, which were reported in **Figure 78b**. The coin cell device shows a specific capacitance of 100 Fg⁻¹ at 0.5 Ag⁻¹.

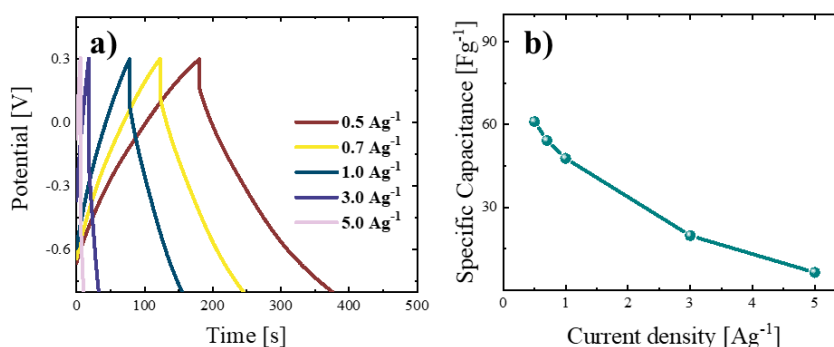


Figure 78 a) GCD curves at different current densities for the asymmetric coin cell based on porous carbon; b) specific capacitance evaluated from GCD discharge curves.

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A strong decrease in the specific capacitance at higher current densities can be observed. To understand the mechanism, we evaluated the iR drop from GCD curves (see **Figure 79a**), and values comparable to the potential window employed were found, explaining the strong decrease of the specific capacitance. In **Figure 79b** we reported the EIS spectrum of the coin cell; here, it is possible to evaluate the uncompensated resistance, which is about $2.1\ \Omega$, and the charge transfer resistance close to $14\ \Omega$ (see Appendix C).

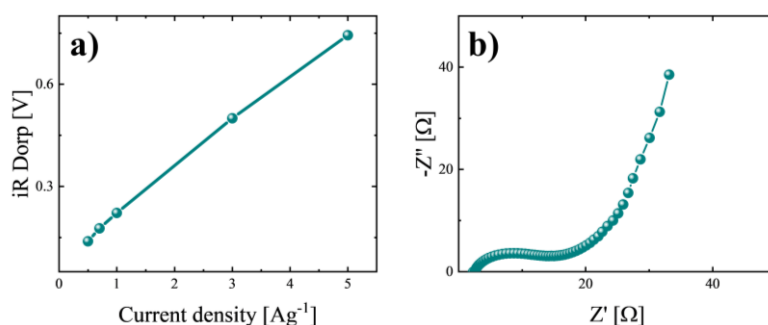


Figure 79 a) iR Drop evaluated from GCD curves for the coin cell based on porous carbon; b) EIS data of the coin cell device.

This section shows a first important step to increase the TRL of the conducted research, indeed a working device was built, which is characterised by performance comparable with the state-of-the-art. All this was done without the addition of any binders for the WE, within an environmentally friendly electrolyte and synthesising the WE from recycled material.

Coin cell based on MoS₂-nanosheets: a device for technological transfer

5.4 Coin cells devices with recycled porous carbon

In the previous section a solid system was obtained, but a further step was done to improve the performance of the assembled coin cell. The scheme for the device was the same seen in **Figure 75**. “Electrode-” was changed, employing a porous carbon material obtained by recycled waste, checking its performance in 1M (NH₄)₂SO₄ we seen a behaviour close to the previous one (see **Figure 76**), hence a rectangular shape, but the current densities reached are higher and calculated specific capacitance is about 200 Fg⁻¹, hence a more active material respect to the commercial porous carbon.

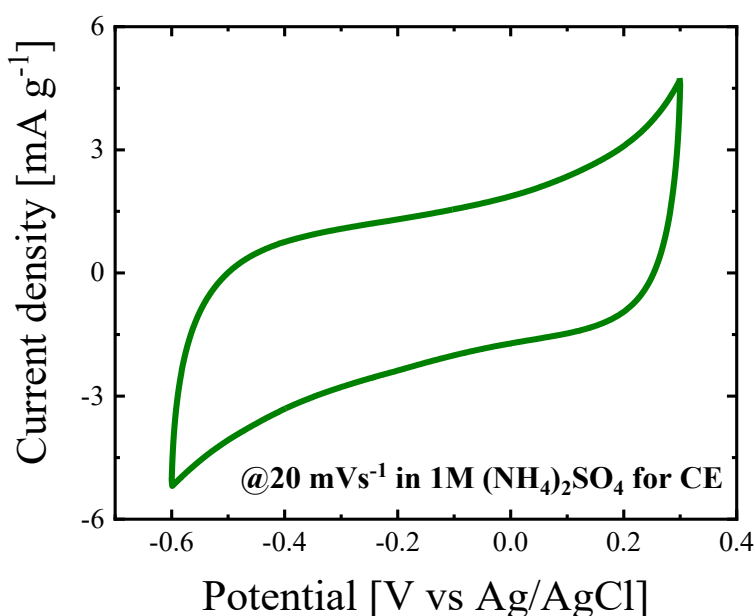


Figure 80 CV of the recycled porous carbon at 20 mVs⁻¹ in 1M (NH₄)₂SO₄.

Then, the coin cell with the recycled porous carbon was assembled, again filling it with 100 μL of 1M (NH₄)₂SO₄. CVs at different scan

Coin cell based on MoS₂-nanosheets: a device for technological transfer

rates were recorded (see **Figure 81a**), where it is possible to observe how the shape varies from leaf to a rectangular, suggesting a supercapacitor behaviour for the device. Eq.6 (see Appendix A) was employed again for the evaluation of the specific capacitance for each scan rate. In **Figure 81b** the results are reported, a promising specific capacitance of about 400 Fg⁻¹ at 5 mVs⁻¹ was calculated, and a specific capacitance of about 200 Fg⁻¹ at 100 mVs⁻¹, hence increasing the scan rates, there is a lower decrease of the specific capacitance with respect to the previous device.

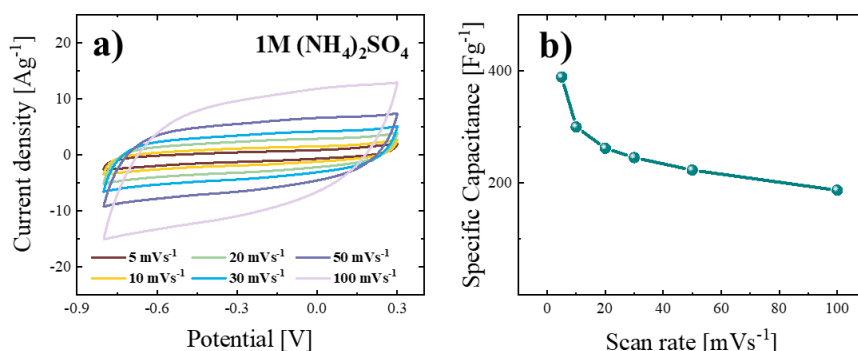


Figure 81 a) CVs at different scan rates were recorded for the asymmetric coin cell based on recycled porous carbon; b) specific capacitance values were evaluated for each scan rates.

To further study the electrochemical behaviour of the device, GCD data were plotted (see **Figure 82a**). This coin cell works at higher current density values with respect to the previous one, and it shows quasi-triangular shape for the curves. This is another insight which link the device to a supercapacitor device. Eq.11 was used to evaluate the specific capacitance by calculating the area under the discharge curve. Studying the results, reported in **Figure 82b**, a higher value for the specific capacitance can be seen, for instance, from 45 Fg⁻¹ at 1 Ag⁻¹ for the previous coin cell; now the value is about 300 Fg⁻¹. It was possible to evaluate the specific capacitance of about 70 Fg⁻¹ at 10 Ag⁻¹.

Coin cell based on MoS₂-nanosheets: a device for technological transfer

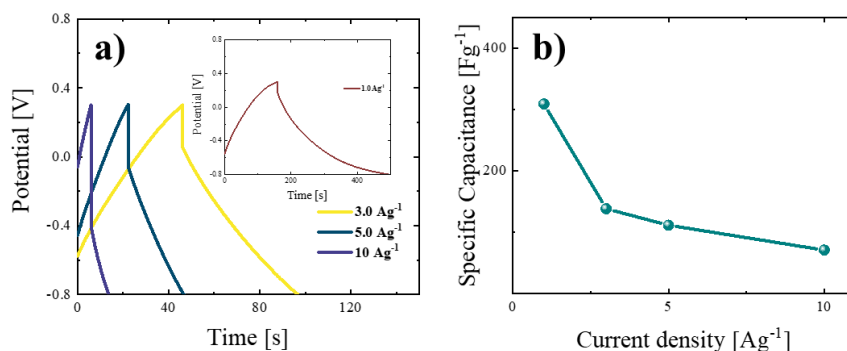


Figure 82 a) GCD curves at different current densities for the asymmetric coin cell based on recycled porous carbon; b) specific capacitance evaluated from GCD discharge curves.

The GCD curves reported in **Figure 82a** were also used to evaluate the iR drop (see **Figure 83a**), which is definitely lower than the previous coin cell; indeed, it reached a value of about 0.75Ω against the 0.35Ω of the new coin cell. The EIS spectrum of the new coin cell is reported in **Figure 83b**, an uncompensated resistance of about 2Ω was evaluated, with a charge transfer resistance of 14Ω (see Appendix C), values comparable to the previous device, but in this case there is a higher impedance in the low frequency region, suggesting that the diffusion as a more important role in this case respect to previous one.

Coin cell based on MoS₂-nanosheets: a device for technological transfer

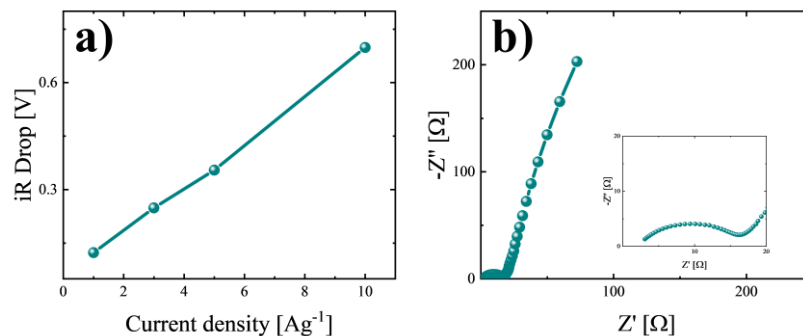


Figure 83 a) iR Drop evaluated from GCD curves for the coin cell based on porous carbon; b) EIS data of the coin cell device.

Durability tests were also performed on the coin-cell device, as shown in **Figure 84**. The results indicate that the specific capacity retains 35% of its initial value after 100 cycles. Since no binders were added, the durability is strongly affected; for this reason, we are currently evaluating different deposition techniques to improve the adhesion and stability of the active material on the substrate, while still avoiding the use of binders.

Coin cell based on MoS₂-nanosheets: a device for technological transfer

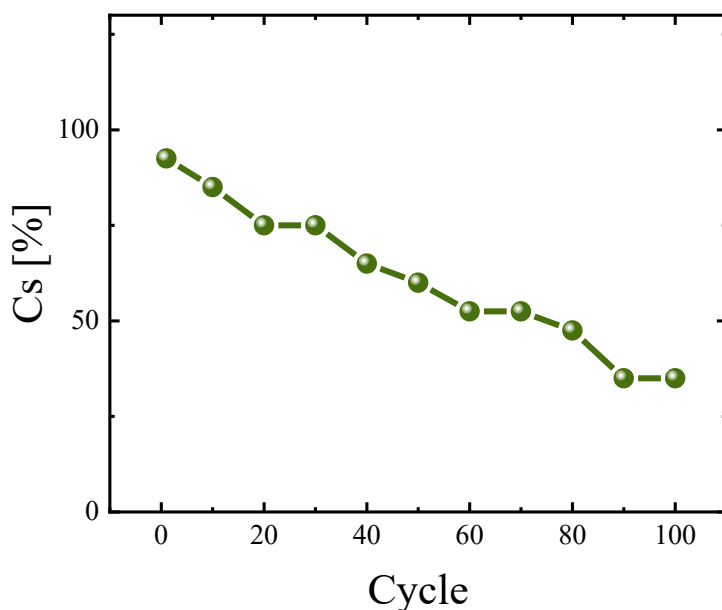


Figure 84 The specific capacitance was evaluated over 100 cycles to observe possible losses of performances.

Energy and power densities were evaluated using Eq.15 and Eq.16 (see Appendix A), building a Ragone plot (see **Figure 85**) to compare the coin cell with other work in the literature. **Table 12** reports the values and works employed to perform the comparison. This is a promising result, indeed, as just said, no binder was added to MoS₂-nanostructures, and no further treatments were performed to increase the electrochemical performance. The increased performance is linked to the proper combination of the two electrodes, the good morphology of the sample and the ammonium-based electrolyte.

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Table 12 Comparison with other two-electrodes devices based on MoS₂ catalysts.

Material	Electrolyte	C _s [Fg ⁻¹]	J [Ag ⁻¹]	E _d [Wh kg ⁻¹]	P _d [W kg ⁻¹]	Referenc e
1T@2H-MoS₂ nanosheets MoS₂@3D graphene network 3D MoS₂ microflowers	1M (NH ₄) ₂ SO ₄	309	1	52	550	This work
	3M KOH	29	1	1	8000	[216]
	PVA/KOH gel electrolyte	243	0.5	1	2400	[217]
MoS₂@Polyaniline	1M (NH ₄) ₂ SO ₄	220	1	60	725	[62]
MoS₂@Graphene Composite	1M Na ₂ SO ₄	2	0.25	2	432	[218]
CuCo₂S₄@ MoS₂	1M NH ₄ Cl	295	1	83	500	[214]

Coin cell based on MoS₂-nanosheets: a device for technological transfer

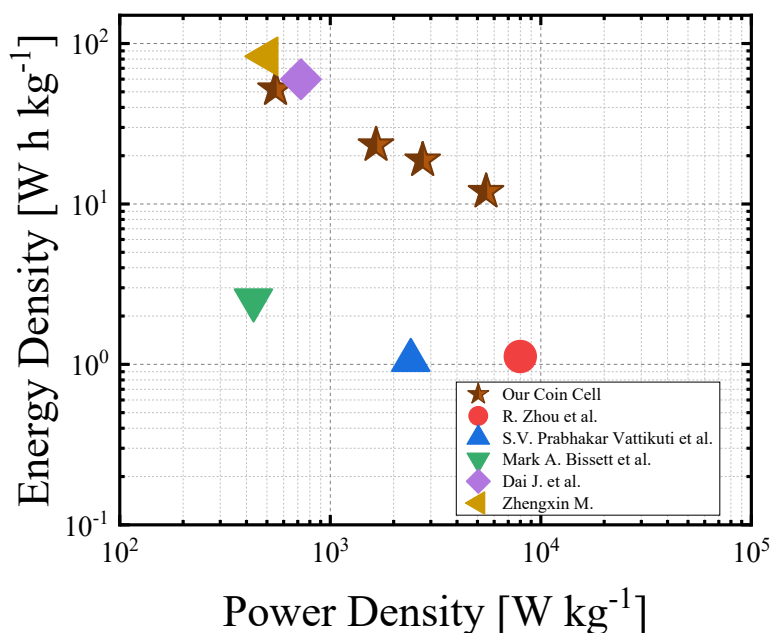


Figure 85 Ragone plot of the coin cell device assembled using recycled porous carbon, it is compared with other works which employ only MoS₂ for the working electrode.

5.5 Conclusions

In this Chapter, an advancement of TRL for the research presented in **Chapter 4** was reported. Firstly, the variation of the substrate shows its importance and how everything can be optimised to improve the overall device. It was seen how the substrate also influences the active mechanisms. First, an improvement of the specific capacitance was observed, from 300 to 1200 Fg⁻¹, at 5 mVs⁻¹. The ECSA increases from 1.6 · 10³ to 10.6 · 10³ cm², suggesting that carbon paper favours ion diffusion, enhancing the storage capacity. Also, GCD measurements confirm the advantages of carbon paper; here, a specific capacitance of

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280 Fg⁻¹ at 5 Ag⁻¹ was obtained, compared with 50 Fg⁻¹ at 5 Ag⁻¹ recorded using graphene paper as substrate. Then, moving from a three-electrode setup to a two-electrode device, an important step was taken; indeed, this transition means passing from a proof-of-concept setup to the validation of what was seen before in a relevant one. The first attempt to assemble a coin cell device employing MoS₂-based nanostructures as the working electrode, without the addition of any binder, and commercial porous carbon as the counter/reference electrode. This device works as a supercapacitor; specific capacitance values of 165 and 100 Fg⁻¹ were evaluated at 5 mVs⁻¹ and 0.5 Ag⁻¹, respectively. The Ragone plot shows how the performance is comparable with the state-of-the-art for MoS₂-based without the addition of activated carbon-based powder. Finally, we changed the counter/reference electrode; a recycled porous carbon was employed to assemble the coin cell. This device has shown promising results - 400 and 300 Fg⁻¹ at 5 mVs⁻¹ and 1 Ag⁻¹, respectively- superior to other works in the literature, also working at higher current densities - reaching 70 Fg⁻¹ at 10 Ag⁻¹- and maintaining low uncompensated and charge-transfer resistances – 2 and 14 Ω, respectively. With respect to the first coin cell, the one based on commercial porous carbon, the second has a more important ion-diffusion mechanism at lower frequencies.

The results presented in this Chapter show the application in a relevant environment for the material synthesised in **Chapter 2** and characterised in **Chapter 4**. These insights can strongly open the way for the widespread employment of recycled materials to develop more sustainable devices. Combining higher performance and the circular economy.

Chapter 6. Conclusion and perspective

This thesis aimed to demonstrate the feasibility of employing recycled materials for energy applications, ranging from water splitting to energy storage. Hence, this work reflects the field's multidisciplinary nature, combining aspects such as circular economy and electrochemistry.

In **Chapter 2**, three different syntheses of various nanostructures were presented. First, orthorhombic MoO_3 (α - MoO_3) nanobelts (50x200nm along 10 μm) were synthesised, employing a one-step hydrothermal process, directly from Mo-based recycled powder. Lower pH values favoured the formation of a well-defined morphology and crystalline phase, promoting preferential growth along the c-axis during the hydrothermal treatment. Collecting XRD patterns, Raman and UV-Vis spectra, we were able to track the shift from Mo-based recycled powder to pure α - MoO_3 . Second, mixed material $\text{MoS}_2/\text{MoO}_3$ -nanostructures were obtained by sulfurising the MoO_3 -nanobelts. Here, the effect of the ratio between the MoO_3 -nanobelts and the Thiourea, as well as the role of nanostructuring of the starting powder, was studied. The absence of well-defined morphologies was recorded for the synthesised materials. Employing different characterisation techniques (e.g., XRD and UV-Vis), different Mo species were observed to coexist in the samples. Firstly, we evaluated the presence of sulphur using the RBS spectrum, finding its typical peak at 1.2 MeV. Then, Raman spectra highlight the presence of both 2H- MoS_2 and α - MoO_3 , offering potential advantages for electrochemical applications. Also, HRTEM images confirm the hexagonal symmetry of the MoS_2 . Third, MoS_2 -nanosheets were produced directly from Mo-based recycled powder, with the role of both pH and synthesis temperature carefully investigated. For instance, increasing the temperature led to larger average nanostructure

Conclusion and perspective

sizes, while lowering the pH resulted in their reduction, as confirmed by SEM images. The phase, however, was not affected by changes in pH or temperature, as shown by different techniques. Indeed, XRD patterns of the samples show the 2H-MoS₂ characteristic peaks at (002), (100) and (101). Also, Raman spectra confirm the presence of 2H-MoS₂; all the samples reported the typical peaks around 375 and 400 cm⁻¹, E_{2g}¹ and A_{2g}, respectively. Moreover, broadening and shifting effects associated with nanostructuring hindered phase identification by XRD and Raman Spectroscopy. Distinguishing between 1T-MoS₂ and 2H-MoS₂ was not possible with conventional techniques, also due to the presence of MoO₃ in the starting material, which exhibits XPS signals close to those of 1T-MoS₂. Nonetheless, XANES spectra provided valuable insights: the strong overlap of the curves suggested the presence of similar phases, and they resembled those reported in the literature and linked to 1T and 2H phases for MoS₂. Overall, this Chapter demonstrated the possibility of obtaining nanostructures from recycled material.

In **Chapter 3**, the synthesised materials were employed for different applications. The electrochemical performance of MoO₃-nanobelts and MoS₂/MoO₃-nanostructures were evaluated for Oxygen Evolution Reaction (OER) and Hydrogen Evolution Reaction (HER), respectively. Here, the effects of different growth parameters were correlated with the electrochemical performance. MoO₃-nanobelts obtained from more acidic solutions exhibited not only a well-defined phase and morphology, but also lower OER overpotential and higher mass activity in alkaline electrolyte— 324 mV and 1.2·10⁻² A mg⁻¹ at 10 mA cm⁻² in 1M KOH, respectively. For HER, the mixed MoS₂/MoO₃ material was studied, revealing that a MoO₃-nanobelts/Thiourea ratio equal to 5 ensured a good balance between the species, enhancing the HER activity compared to the starting material. In this case, a promising overpotential of 208 mV was found at 10 mA cm⁻² in 1M H₂SO₄, with

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a mass activity of $0.3 \cdot 10^{-2} \text{ A mg}^{-1}$. Once characterised, the two materials were integrated into an overall water splitting cell in 1M KOH, requiring 1.9 V to operate, with a Tafel slope of 57 mV dec^{-1} . Although further optimisation is needed, this result represents an important milestone and demonstrates the feasibility of employing recycled materials in this field.

Chapter 4 focused on energy storage applications, particularly involving NH_4^+ , which represents a promising solution for future systems. Firstly, a deeper investigation of the active mechanisms in MoO_3 -nanobelts was carried out by varying the electrolyte. As learned from previous experiments, MoO_3 -nanobelts performed better in alkaline environments; thus, 1M NH_4OH and 1M KOH were selected to study the effect of the electrolyte. A detailed comparison was carried out, highlighting the differences between NH_4^+ and K^+ ions. Firstly, moving from NH_4OH to KOH, a transition from pseudocapacitive to supercapacitive behaviour was observed. The calculated specific capacitance decreases from 300 to 100 Fg^{-1} at 5 mVs^{-1} passing from potassium hydroxide to ammonium hydroxide. The interaction between NH_4OH and MoO_3 -nanobelts likely produced a passivation layer at the interface, activating resistive mechanisms, as also indicated by iR drop and Phase plot analyses, which show an increase in the sample resistance moving to NH_4OH . One of the main goals of this Chapter was to study NH_4^+ storage, for which MoS_2 -nanosheets synthesised in **Chapter 2** were used. These nanostructures were characterised in a 3-electrode setup with 1M $(\text{NH}_4)_2\text{SO}_4$ as electrolyte, which is considered environmentally friendly while enabling the study of NH_4^+ storage. No binders were employed in the electrode preparation, providing a comprehensive understanding of the material's active mechanisms. In this case, the effects of pH and hydrothermal temperature were evaluated, showing that their combined optimisation significantly improved electrochemical measurements. In particular, the SR_200_1.1

Conclusion and perspective

sample, obtained by tuning both parameters, exhibited a specific capacitance of 300 and 200 Fg^{-1} at 5 mVs^{-1} and 0.5 Ag^{-1} , respectively; outperforming the SR_180_2.4 sample, and showing lower performance losses at higher scan rates and current densities. The sample SR_200_1.1 also showed a superior ECSA compared to others, equal to $1.74 \cdot 10^3 \text{ cm}^2$, and a lower iR drop, about 0.05 V at 5 Ag^{-1} , consistent with the different morphologies of the samples. Still, SR_200_1.1 reports a lower contact resistance (2.1 Ω) was recorded.

In **Chapter 5**, the research moved a step beyond, developing a device prototype, and gained an important understanding of the active mechanisms, thus increasing the technology readiness level (TRL). Prototypes based on SR_200_2.4 were fabricated and tested in relevant setups. First, the influence of the substrate on the electrochemical performance of the material was demonstrated, revealing a significant improvement from 300 to 1200 Fg^{-1} at 5 mVs^{-1} . Then, two types of coin cells were assembled, the first employing commercial activated carbon, and the second one using recycled porous carbon. The former exhibited performances comparable with the state-of-the-art devices, with a specific capacitance of 175 Fg^{-1} at 5 mVs^{-1} , while the latter outperformed it, reaching 400 Fg^{-1} at 5 mVs^{-1} . The second device showed a specific capacitance of 100 Fg^{-1} at 5 Ag^{-1} , higher than the previous, which reported 25 Fg^{-1} at 5 Ag^{-1} . The second one was also studied at 10 Ag^{-1} , reaching a specific capacitance of 70 Fg^{-1} . Both devices operated as supercapacitors, as confirmed by various analyses, demonstrating promising potential for future applications. Further steps are under evaluation to improve this research. In particular, device durability is being investigated while still avoiding the use of binders. This goal can be achieved through the employment of in operando techniques, which allow monitoring of material evolution during measurements, providing deeper insights that can guide improvements in the preparation.

Appendix A. Characterization techniques

Morphological and phase characterization

As first analysis, the samples usually were morphologically characterized using a Scanning Electron Microscope (SEM) Gemini Field Emission SEM Carl Zeiss SUPRATM 25 (FEG-SE, Carl Zeiss Microscopy GmbH, Jena, Germany) set to In-Lens mode. This technique allows the study of the morphology for all the samples, from MoO₃-nanobelts to MoS₂-nanosheets, reported in Chapter 2.

In Chapter 2 The transmittance measurements on MoO₃-nanobelts and MoS₂/MoO₃-nanostructures were shown, they were performed using a PerkinElmer UV/Vis/NIR Spectrometer Lambda 1050+ between 250 and 800 nm, with steps equal to 2 nm. The transmittance was used to evaluate the product between the absorption coefficient and the thickness of the sample, to do that the Beer-Lambert law was employed [136]:

$$\alpha t = \ln \left(\frac{1}{T} \right) \quad \text{Eq. 1}$$

where α is the absorption coefficient, t is the equivalent thickness of nanostructures, and T is the recorded transmittance. Then, the product αt was used to build the Tauc plot, which consists on plot $(\alpha h\nu)^{1/n}$ vs $h\nu$, with n that assumes different values depending on the type of bandgap, $\frac{1}{2}$ and 2, respectively for direct and indirect bandgap [137].

The Raman spectra for all the samples were recorded through a Horiba Scientific instruments model 1024X256-OE, with a laser by THORLABS model HNL225R with a wavelength of 633 nm. This

Characterization techniques

technique allows to study the chemical footprint of the sample, recording also structural insights about the studied materials.

Again, in Chapter 2 the presence of Mo, O and S in the synthesized materials was evaluated by Rutherford Backscattering Spectrometry (RBS), using a 2.0 MeV He^+ beam at normal angle incidence, accelerated by a 3.5 MV High Voltage Engineering Europa (HVEE) Singletron accelerator system. RBS was performed by collecting backscattered ions at 165° off the axis, and spectra were analyzed using XRump software (Thompson M., Windows (95-Win7)-Genplot and RUMP, Available online, <http://www.genplot.com/download.htm>). The RBS analysis, which is schematized in **Figure 86**, uses a ion beam gun to hit the sample and it records the energy backscattered ions to study the species. It is possible to observe contaminations, and the ratio of the materials present on the substrate.

Characterization techniques

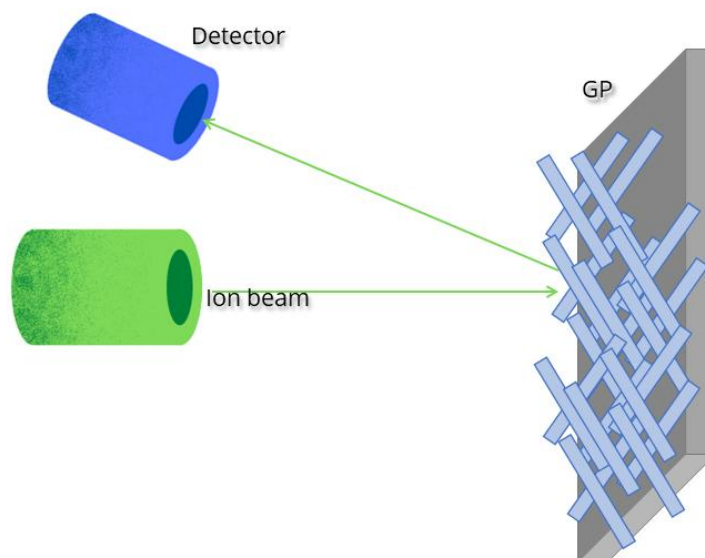


Figure 86 Schematization of RBS analysis on MoO₃-nanoblets, with Graphene Paper as substrate.

MoS₂/MoO₃-nanostructures, reported in Chapter 2, were transferred from the substrate directly on the TEM grid for TEM characterization by mechanical rubbing. The obtained specimens were examined using a Cs-probe-corrected TEM JEOL ARM200CF microscope, operated at 200 keV in scanning-TEM (STEM) mode. While, to study MoS₂-nanosheets, High-resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM) and electron energy-loss spectroscopy (EELS) were obtained in an FEI F20 at 200 kV. The HRTEM was acquired with a condenser aperture of 100 μm , no objective aperture, spot size 3, and a BM-UltraScan CCD camera. The STEM–EELS was acquired with a condenser aperture of 70 μm , no objective aperture, nominal camera length 30 mm, spot size 6, and Gatan EF-CCD camera. The EELS supporting STEM images were obtained via an angular dark field detector (DF4).

Characterization techniques

For the crystalline structure of the different materials by X-ray diffraction (XRD) patterns were recorded. For the analysis of MoO₃-nanobelts and MoS₂/MoO₃-nanostructures a Bruker-AXSD50050-θ diffractometer was used, with a Gobel mirror to parallel the Cu Kα radiation operating 40 kV at 30 mA. While, for MoS₂-nanosheets patterns were analysed employing a Bruker AXS D8 Advance X-ray diffractometer with Ni-filtered (2 μm thickness) Cu-Kα radiation (λ= 1.5406 Å) operated at 40 mA and 40 kV.

XRD patterns were also employed to evaluate the Scherrer parameters of the crystals in the materials, they were calculated using the following formula [219]:

$$\tau = \frac{k\lambda}{\beta \cos\theta} \quad \text{Eq.2}$$

where τ is the crystallite size, k is the shape factor (about 0.9), λ is the X-ray wavelength, β is the full width at half maximum and θ the Bragg angle relative to the studied peak. The Raman spectra were acquired using a Horiba Scientific instruments model 1024X256-OE, with a laser by THORLABS model HNL225R with a wavelength of 633 nm.

The surface chemical composition of the samples was investigated by X-ray Photoelectron Spectroscopy (XPS), using a PHI 5000 VersaProbe system equipped with a monochromatic Al Kα radiation source (1486.6 eV), excited by a micro-focused electron beam. Spectra were acquired at a photoelectron take-off angle of 45° with respect to the sample surface. The binding energy scale was referenced to the C 1s peak of adventitious carbon, set at 285.0 eV.

X-ray Absorption Spectroscopy (XAS) data were acquired at the ALBA synchrotron, CLAEISS beamline, under ambient temperature and pressure employing a Si 311 DCM, and an SDD multichannel fluorescence detector. References and samples were run in

Characterization techniques

transmission, prepared as pellets diluted in cellulose. Several scans were acquired to ensure data quality and reproducibility. The Athena software package with the AUTOBK algorithm was used for data processing[220]. The energy was calibrated to the first inflection point of Mo foil taken as 20 keV. Extended X-ray Absorption Fine Structure (EXAFS) spectra were extracted using a spline in the 0-17.9 Å⁻¹ k-range, a R_{bkg} of 1.1, with E0 taken as the maximum of the first derivative.

Electrochemical characterization

The electrochemical measurements were performed using a potentiostat (model VersaSTAT 4, Princeton Applied Research, USA) with a three-electrodes setup. Different types of analysis were done, in Chapter 3 the performances for water splitting reaction were studied, first OER measurements were performed in an alkaline electrolyte (1 M KOH), while for HER an acidic media was employed (1M H₂SO₄). Saturated calomel electrode (SCE) was used as reference electrodes, the counter electrodes were Pt wire and graphite rod, for OER and HER, respectively. The electrodes prepared with Mo-based nanostructures were used as working electrodes. The electrochemical performances of the Mo-based nanostructures were measured by Linear Sweep Voltammetry (LSV), with a scan rate of 5 mV s⁻¹ from 0 to 1.7 V and from 0 to -1 V versus SCE for OER and HER analysis, respectively. The measured potential was converted from SCE to Reversible Hydrogen Electrode (RHE) using the Nernst Equation [29]:

$$E_{\text{RHE}} = 0.241 \text{ V} + E_{\text{SCE}} * \text{pH} * 0.059 \quad \text{Eq.3}$$

where E_{RHE} is the potential versus RHE, 0.241 V is the standard potential of SCE at 25 °C and E_{SCE} is the measured potential versus SCE. Tafel analysis was obtained from the LSV measurements. Electrochemical Impedance Spectroscopy (EIS) analysis was carried out in a potentiostatic mode. An AC voltage with an amplitude of 10

Characterization techniques

mV and frequency that varies from 100 kHz and 10 mHz is superimposed to a constant voltage (which is fixed at the potential at 10 mA/cm²). The uncompensated resistance R_u extracted from EIS curves was used to correct the potential as follows [30]:

$$E_{\text{RHE}}^{\text{corr}} = E_{\text{RHE}} - iR_u \quad \text{Eq. 4}$$

In which i is the measured current [A]. The electrocatalytic activity of the samples has been verified by calculating the mass activity at fixed current densities, which is a useful estimation of the intrinsic activity of electrocatalysts (see Table S1). The mass activity can be calculated with the relation[221], [222]:

$$\text{Mass Activity} = \frac{J}{m_{\text{loaded}}} \quad \text{Eq. 5}$$

J is the current density expressed in A cm⁻² and m_{loaded} the deposited mass load of each electrode in mg cm⁻².

Then, in Chapter 4, we studied the electrochemical performances of the samples for energy storage applications. Here, three-electrode measurements were done using the synthesized materials as working electrode, Ag/AgCl as reference one and a platinum wire as counter electrode. The energy storage tests were executed in 1M ammonium sulphate (1M (NH₄)₂SO₄). Firstly, we performed Cyclic Voltammograms (CV) curves at different scan rates, to evaluate the specific capacitance at each scan rate by using the following equation [223]:

$$C_s = \frac{\int IdV}{mv\Delta V} \quad \text{Eq.6}$$

C_s is the specific capacitance, I the current, m the mass of the electrode, v the scan rate and ΔV the potential range. CV curves were also analysed using Power Law formula to discriminate between surface or diffusion dominant mechanisms [224]:

Characterization techniques

$$i = av^b \quad \text{Eq.7}$$

Here v is the scan rate and i is the current measured at a fixed potential, while a and b are coefficients related to the kinetics of the system; ideally, if ion-diffusion mechanisms dominate the energy storage processes, the current depends on the square root of the scan rate (b equal to 0.5), while if surface mechanisms dominate the energy storage processes, the current depends linearly on the scan rate (b equal to 1).

Dunn's model was employed to evaluate in detail surface-capacitive and ion-limited diffusion contributions for the storage, since, following this model, the measured current can be described as follow [209]:

$$i = k_1 v + k_2 v^{\frac{1}{2}} \quad \text{Eq.8}$$

In the previous formula, i is the current, v is the scan rate, k_1 is the coefficient of the surface-limited contribution, and k_2 is the coefficient to the diffusion-controlled contribution.

Also, we were interested to estimate the effective surface area, which was active for energy storage mechanisms, for this reason we want to evaluate the Electrochemical Surface Area (ECSA), using the following formula [210]:

$$\text{ECSA} = \frac{C_{dl}}{C_s} \quad \text{Eq.9}$$

Where C_s is theoretical specific capacitance for a planar electrode in an aqueous electrolyte (equal to $40 \mu\text{Fcm}^{-2}$ [199]). while C_{dl} is the electrochemical double-layer capacitance. The C_{dl} can be extracted from CVs using the current density values for each scan rate at a fixed potential, and it is evaluated thanks to the following formula [225]:

Characterization techniques

$$J = C_{dl} \nu \quad \text{Eq.10}$$

J is the current density, C_{dl} the double-layer capacitance and ν the scan rate. The storage performances of the samples were also studied using Galvanostatic Charge-Discharge (GCD) curves, from these the specific capacitance can be extracted in different ways depending on the symmetry of the GCD curve, indeed for a triangular one it is possible to use the following formula[226]:

$$C_s = \frac{It_d}{m\Delta V} \quad \text{Eq.11}$$

C_s is the specific capacitance, I the current, m the mass of the electrode, t_d the discharge time and ΔV the range potential. While for non-triangular case we can employ another one [227]:

$$C_s = \frac{2I}{m\Delta V^2} \int_{V_i}^{V_f} V(t) dt \quad \text{Eq.12}$$

C_s is the specific capacitance, I the current, m the mass of the electrode, t_d the discharge time, ΔV the range potential and $\int_{V_i}^{V_f} V(t) dt$ is the area under the discharge curve of the GCD, which take account with the possible non-linearity of the curve [36]. From these curves the IR Drop values were extracted as the difference between the potential at the end of the charge curve and the one at the beginning of the discharge curve, it is linked to the energy loss due to the sample's finite internal resistance. The Internal Resistance values were evaluated for the sample, thanks to IR Drop extracted at each current density, using the following formula [228]:

$$R_i = \frac{V_{charge} - V_{discharge}}{I} \quad \text{Eq. 13}$$

R_i is the internal resistance, I the current, V_{charge} and $V_{discharge}$ are the potential values respectively at the end of the charge and at the beginning of the discharge.

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Electrochemical Impedance Spectroscopy (EIS) analysis was carried out between 100 kHz and 0.1 Hz in a potentiostatic mode using an AC voltage with an amplitude equal to 10 mV. All the measurements superimposed to open circuit voltage, to study the contact resistance (R_c) at the interface with the electrolyte.

In Chapter 5 the MoS₂-based material, which was studied and characterized in Chapter 4, was employed to assemble CR2032 coin cell devices, hence two-electrode ones. In this case the data were recorded another electrochemical workstation (Corrtest, Shanghai, China). The charge balance theory ($Q^+ = Q^-$) was considered for the calculation of the ratio between the anode and the cathode masses as follows [229], [230]:

$$\frac{m_-}{m_+} = \frac{c_{s+} * \Delta V_+}{c_{s-} * \Delta V_-} \quad \text{Eq.14}$$

in which m_- , m_+ , c_{s-} , c_{s+} , ΔV_{+-} , and ΔV_+ are the mass of the electrochemically active materials. Eq.5, Eq.9 and Eq.10 were used again to evaluate the electrochemical performance of the device. To further study the performance of the coin cell and to compare with the state-of-the-art, energy [Wh/Kg] and power [W/Kg] densities (E_d and P_d respectively) of the device were calculated [231]:

$$E_d = \frac{1}{2 * 3.6} * c_s * \Delta V^2 \quad \text{Eq.15}$$

$$P_d = \frac{3600}{\Delta t} * E_d \quad \text{Eq.16}$$

Appendix B. Preparation of the electrodes

Electrodes for water splitting applications

In **Chapter 2** the syntheses of MoO₃-nanobelts and MoS₂/MoO₃-nanostructures were shown, these nanostructures were employed in **Chapter 3** for water splitting application. OER and HER electrodes were prepared by applying the powder of MoO₃-nanobelts and MoS₂/MoO₃ nanostructured electrocatalysts onto graphene paper (GP, Sigma Aldrich, 240 μm thick), which was used as substrate. In detail, 1 mg of nanobelts powder was dispersed in 1 mL of deionized water, and a solution of polyvinylidene difluoride (PVDF, Sigma Aldrich, 50 μL) in acetone (11 $\text{g}\cdot\text{L}^{-1}$) was added. The mixture was sonicated for 30 minutes. PVDF is used as a binder and does not influence the performance of the material, as reported in the literature [232]. The mixture was dropped on a GP substrate and dried at room temperature overnight. The deposited mass was calculated as the difference between the electrode mass after and before the drop-casting and drying steps, by using a Mettler Toledo MX5 Microbalance with a sensitivity of 0.01 mg. The area of the exposed mass was measured for each sample, thus obtaining a mass loading of 0.9 $\text{mg}\cdot\text{cm}^{-2}$ for MoO₃-nanobelts. MoS₂/MoO₃ nanostructures were directly drop casted on GP substrate without any binder, with a catalyst loading of about 3 $\text{mg}\cdot\text{cm}^{-2}$.

Electrodes for energy storage applications

Again, in Chapter 2 different syntheses of MoS₂-nanosheets were studied. Then, the resulting solutions were a sort of black ink, and they were used to realize electrodes for the electrochemical characterization for energy storage purpose. The samples in **Chapter 4** the inks were drop casted on a substrate of Graphene Paper (GP, Sigma Aldrich, 240 μm thick); the sample was dried at room temperature for a night. The

Preparation of the electrodes

deposited mass was evaluated by taking the difference between the dried sample and bare substrate mass, by using a Mettler Toledo MX5 Microbalance with a sensitivity of 0.01 mg. The catalyst loading was fixed to 1.3 mg cm^{-2} , on an area of 1.1 cm^2 .

Electrodes for coin cell devices

In **Chapter 5** the assemble of a coin cell device is described, this goal was obtained thanks to both variation of the substrate and preparation of carbon-based electrodes. The preparation was the same, indeed the material was again dropped on the substrate, without the addition of any binder, and dried overnight. The novelty is the substrate, a Carbon Paper (CP, AvCarb EP40, FuelCell Store, $200 \text{ }\mu\text{m}$ thick). The coin cells were also characterised by a counter/reference electrode, which was prepared using a carbon-based slurry, obtained mixing activated carbon by Sigma-Aldrich with Polyvinylidene fluoride, with a ratio of 90:10 respectively, then the powder was wetted adding about $350 \text{ }\mu\text{L}$ of N-methylpyrrolidon (NMP). Then, the slurry was deposited on aluminium foil, and using a doctor blade it was spread on the substrate. Finally, the aluminium foil was transferred to an oven at $60 \text{ }^{\circ}\text{C}$ overnight, the NMP dried slowly within the oven, favouring a superior stability of the electrode. The foil was cut in 16 mm disks, which are compatible with the CR2032 case of the coin cells. Still in **Chapter 5** a new coin cell was assembled, substituting the commercial activated carbon with a porous carbon synthesised by recycled material. The process was the same described for the previous one.

Appendix C. EIS measurements and their versability

Electrochemical Impedance Spectroscopy (EIS) data were widely employed during this thesis work, they give important insights about the samples. Here, in this Appendix, three possible applications for the EIS data will be presented. In the first case the Nyquist plot was directly studied, while, in the other two cases, different equivalent circuits were employed for the fitting of EIS spectra, due to different experimental conditions.

The iR_u -correction

During electrochemical measurements the position between working and reference electrodes can affect the kinetics of the charges, for this reason it is important to evaluate the uncompensated resistance (R_u), which take account of this correction [233]. The R_u can be easily evaluated taking the intercept with the x-axis, which corresponds to the high-frequency region of the Nyquist plot using Eq.4 (see Appendix A) [234]. In **Chapter 3** we performed Linear Sweep-Voltammetry (LSV) measurements for MoO_3 -nanobelts and $\text{MoS}_2/\text{MoO}_3$ -nanostructures both OER and HER, then EIS spectra were recorded, to evaluate the R_u . **Figure 87** reports the EIS spectra recorded for MoO_3 -nanobelts at the OER potential. The extracted values are reported in **Table 13**, showing a decrease of the uncompensated resistance when the ratio of hydrogen peroxide increases.

Table 13 R_u values extracted from the Nyquist plot for the MoO_3 -nanobelts for OER.

Sample	R_u [Ω]
N0	5.2
N7	4.7
N14	4.3
N18	3.4

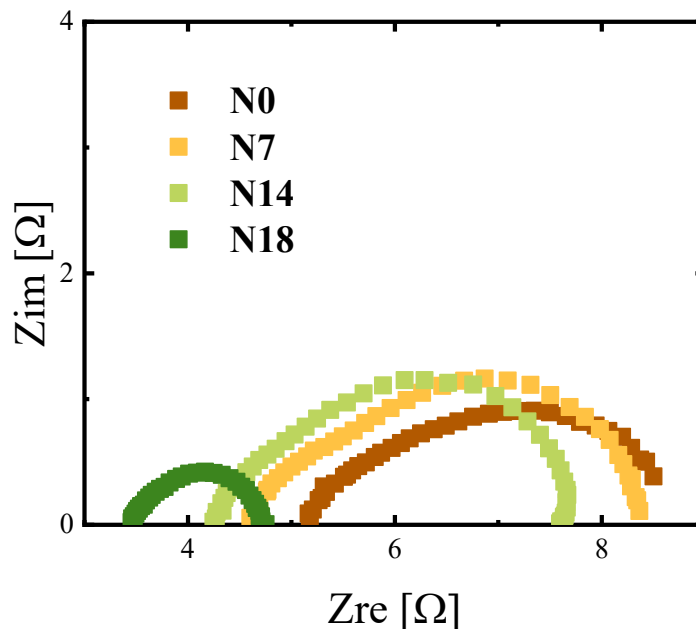


Figure 87 EIS measurements for N0, N7, N14 and N18 samples, for $Z_{im}=0$ it was extracted Z_{re} value that corresponds to the uncompensated resistance.

In **Figure 88** the EIS spectra of the $\text{MoS}_2/\text{MoO}_3$ -nanostructures are reported, they were evaluated at HER potential to correct their LSV curves. The spectra are compared with N18 one registered for HER application, a different shape can be observed, suggesting that the sulfurization produced effect on the kinetics of the samples. The extracted values are reported in **Table 14**, SN2.5 and SN7.0 registered a lower uncompensated resistance at the interface, than samples SN5.0 and SR5.0.

EIS measurements and their versability

Table 14 R_u values extracted from the Nyquist plot for the MoS₂/MoO₃-nanostructures for HER.

Sample	R_u [Ω]
N18	6.1
SN2.5	2.7
SN5.0	9.1
SN7.0	2.7
SR5.0	6.1

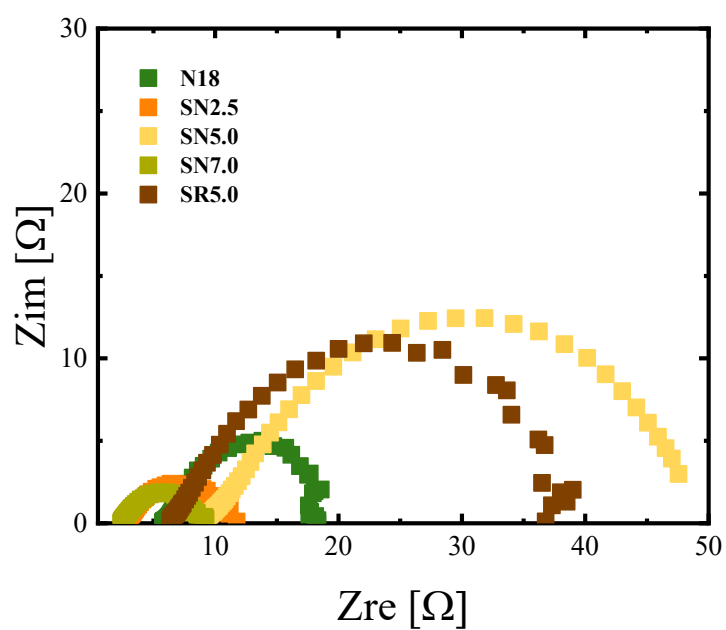


Figure 88 EIS measurements for synthesis SN2.5, SN5.0, SN7.0 and SR5.0 for $Z_{im}=0$ it was extracted Z_{re} value that corresponds to the uncompensated resistance.

Mott-Schottky and Electrochemical Impedance Spectroscopy

The Mott-Schottky measurements usually were performed to study the interaction between flat interface and the electrolyte, extracting information like flat band potential and donor concentration. The parameters were extracted thanks to the Mott-Schottky (MS) relation [235], [236]:

$$\frac{1}{C^2} = \frac{2}{\epsilon_0 \epsilon_r e A^2 N_D} \left(E - \frac{k_B T}{e} - E_{FB} \right) \quad \text{Eq. 17}$$

Where N_D is the donor concentration and E_{FB} is the flatband potential, A^2 is the square of the electrode area, ϵ_0 is the dielectric constant in the vacuum, ϵ_r is the relative dielectric constant, k_B is the Boltzmann constant, T the temperature, e the electron charge and E the applied potential. Considering the above relation, the donor concentration can be extracted from the slope of the linear region, while the flatband potentials is calculated subtracting the open circuit voltage to the intercept with the x-axis of the linear region. The MS technique require flat surface, for this reason its application for nanostructured electrode is challenging, but according to Sivula there are three hypotheses to validate the Mott-Schottky measurements on a nanostructured electrode, which are the following [237]:

1. Is the extracted N_d physically reasonable?
2. From MS measurements it is possible to extract the depletion region width, using the following formula [238]:

$$W = \sqrt{\frac{2\epsilon_r \epsilon_0 (E - E_{FB})}{e N_d}} \quad \text{Eq.18}$$

Where W is the width of the depletion region, ϵ_r is the relative dielectric constant, ϵ_0 is the dielectric constant in vacuum, E stands for the applied potential, e the charge of the electron, N_d and E_{FB} are respectively the donor concentration and the flat

EIS measurements and their versability

band potential extracted from measurements. Is the calculated W comparable or lower than the average size of the nanostructures?

3. Is capacitance extracted from EIS fitting comparable with the ones of the MS measurements?

MS measurements on MoO_3 -nanobelts were performed from -1.0 to -0.2 V versus SCE at 1000 Hz, and they are reported in **Figure 89**. Hence, the electrode interface has an intrinsic roughness due to the presence of nanostructures, for this reason the validation was operated using the three hypotheses of Sivula. From the intercept with the x-axis the flat band potential was evaluated, about -1.11 V. From the slope it was estimated the donor concentration, it is equal to $1.18 \cdot 10^{22} \text{ cm}^{-3}$, which comparable to other oxides as Fe_2O_3 which is about 10^{21} cm^{-3} [239]. Then, the Eq.18 it was employed to evaluate the size of the depletion region, it is about $0.9 \cdot 10^{-9} \text{ m}$, which is three orders of magnitude lower than the nanobelts size, hence it is physically consistence.

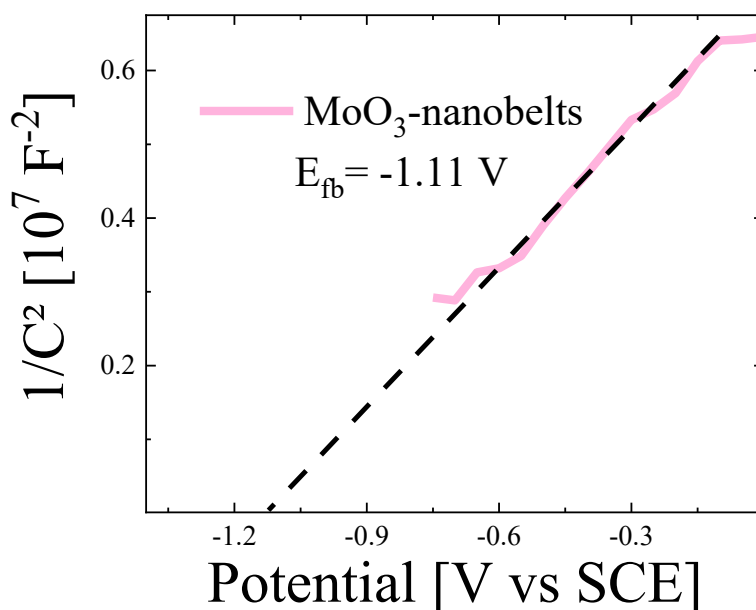


Figure 89 Mott-Schottky measurements for MoO₃-nanobelts.

The last validation was done performing the EIS fitting (see **Figure 90**), using the equivalent circuit suggested by Sivula[237], but the capacitor were simulated using two Constant Phase Element (CPE); due to the roughness linked to the nanostructured nature of the electrode, CPE helps to describe the non-ideal capacitor behaviour [240]. The extracted C_{sc} is reported in **Table 15** together with the other fitting parameters and their percentage error, its value is about 10^{-3} F, which is close to the experimental one, as requested to validate the MS data.

EIS measurements and their versability

Table 15 Fitting parameters of MoO₃-nanobelts EIS spectrum.

Circuit Element	Value	Err [%]
C_{sc}	10^{-3} F	18.37
n_1	0.81	2.73
C_{ss}	$2 \cdot 10^{-3}$ F	39.1
n_2	0.78	5.94
R_s	3.45Ω	0.69
R_B	0.4Ω	9.9
R_{ct}	0.9Ω	6.98

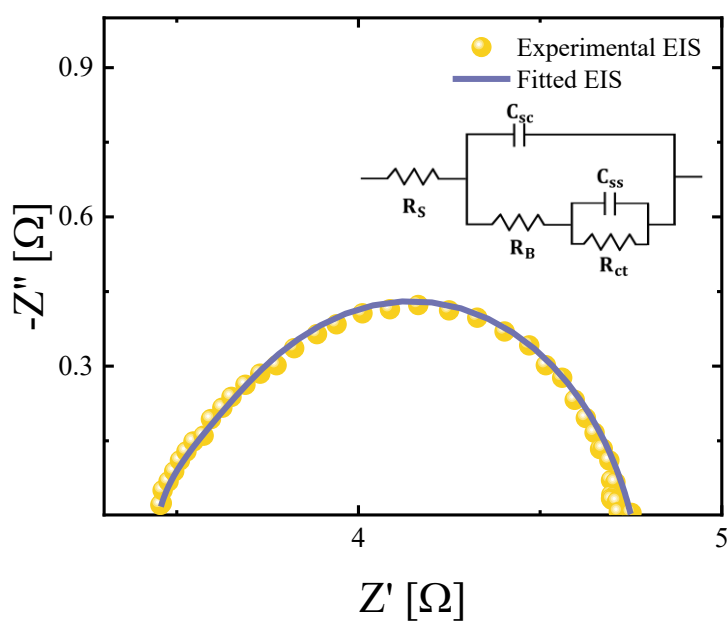


Figure 90 EIS experimental data with the fitted curve and the equivalent circuit employed.

EIS measurements and their versability

EIS spectrum of assembled coin cell

The assembled coin cell in Chapter 5 was also studied using EIS data, but the Nyquist plot can be hard to study and separate the different contributions. In many works the Bode plots are employed to distinguish the mechanisms, both Magnitude [196] and Phase [197] plots. A possible alternative to study directly the Nyquist or Magnitude plots can be the extrapolation of the Distribution of Relaxation Time (DRT) using DRTtools algorithm to distinguish the different mechanism [241]. The DRTtools algorithm fits the experimental data to a Voigt equivalent circuit, which consist of an infinite series of RC circuit, through the following formula [242]:

$$Z_{DRT} = R_{\infty} + \int_0^{\infty} \frac{\gamma(\ln\tau)}{1+i2\pi f\tau} d\tau \quad \text{Eq.19}$$

Where Z_{DRT} is the fitted impedance, $\gamma(\ln\tau)$ the distribution function of the relaxation times, f the frequencies, τ the relaxation times and R_{∞} is the ohmic resistance. Thanks to the algorithm it is possible to evaluate $\gamma(\ln\tau)$, which is proportional to the system resistance, as a function of τ . This method links each mechanism to a RC circuit, hence to a characteristic time, this produces a peak in $\gamma(\ln\tau)$ plot, and its area weight the mechanism during the measurements [5].

Before to perform EIS fitting and DRT calculation, Kramers-Kronig Validation was done using a homemade Python code employing the algorithm reported by Macdonald et al. [243], based on the following integral transform:

$$Z_{Im}^{KK}(\omega) = -\frac{2\omega}{\pi} \int_0^{\infty} \frac{Z_{Re}(\omega') - Z_{Re}(\omega)}{\omega'^2 - \omega^2} d\omega' \quad \text{Eq.20}$$

$$Z_{Re}^{KK}(\omega) = R_{\infty} + \frac{2}{\pi} \int_0^{\infty} \frac{\omega' Z_{Im}(\omega') - \omega Z_{Im}(\omega)}{\omega'^2 - \omega^2} d\omega' \quad \text{Eq.21}$$

Then, we calculated the residuals for both imaginary and real impedance using the following equations:

EIS measurements and their versability

$$\text{Res}(Z_{\text{Im}}(\omega)) = \frac{|Z_{\text{Im}}^{\text{KK}}(\omega) - Z_{\text{Im}}(\omega)|}{Z_{\text{Im}}(\omega)} \quad \text{Eq. 22}$$

$$\text{Res}(Z_{\text{Re}}(\omega)) = \frac{|Z_{\text{Re}}^{\text{KK}}(\omega) - Z_{\text{Re}}(\omega)|}{Z_{\text{Re}}(\omega)} \quad \text{Eq. 23}$$

A threshold was fixed at 90%, for residual exceeding this value, the EIS interpretation becomes unreliable. The result is reported in **Figure 91**, in which an increasing in the percentage error for low frequency, this can be linked to cable issues [240].

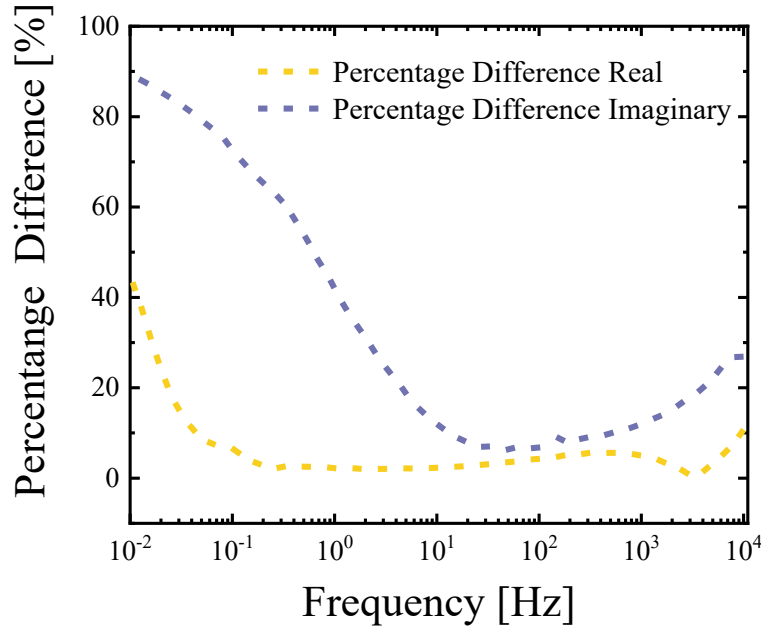


Figure 91 Plot of the percentage difference for real and imaginary part.

The $\gamma(\ln\tau)$ distribution report different peaks, to facile the assignment of the peaks an EIS fitting was performed (see **Figure 92**), the fitting parameters are reported in **Table 16**. The employed equivalent circuit is a combination of a Randle circuit and a circuit in series, composed

EIS measurements and their versability

by a CPE and a Warburg element in parallel, this added circuit help to take account the substrate employed to build the electrode, as done by Tsyganov et al. [207].

Table 16 Fitting parameters of MoO₃-nanobelts EIS spectrum.

Circuit Element	Value	Err [%]
R_u	2.1 Ω	3.7
R_{ct}	13.9 Ω	0.5
CPE1	6 F	5.5
n₁	4*10 ⁻⁴	2.4
W₁	0.7 Ω	0.4
CPE2	2*10 ⁻³ F	25.6
n₂	0.25	28.6
W_{OR}	2.7 Ω	0.8
W_{OC}	0.3 Ω	5.1

EIS measurements and their versability

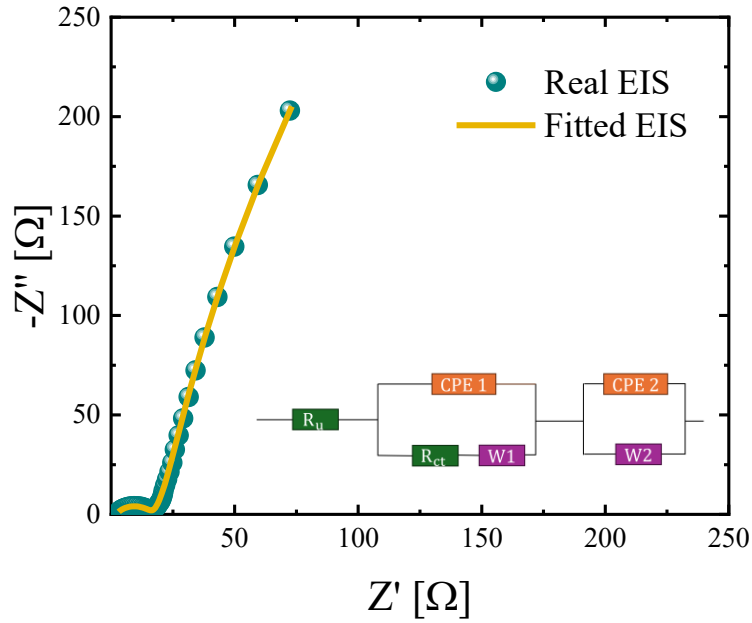


Figure 92 Experimental data with fitted curve, together with the equivalent circuit.

Then, an assignment of the peaks was done, as shown in **Figure 93**, helping with the EIS fitting. The peak for $10^0 \text{ s} < \tau < 10^1 \text{ s}$ is linked to the charge-transfer resistance, while between $5 \cdot 10^{-3} \text{ s}$ and 10^0 s the peaks can be related for the double-layer formation, at the end the peak at 10^{-4} s is due to fast reaction linked to the interface electrode-electrolyte [244].

EIS measurements and their versability

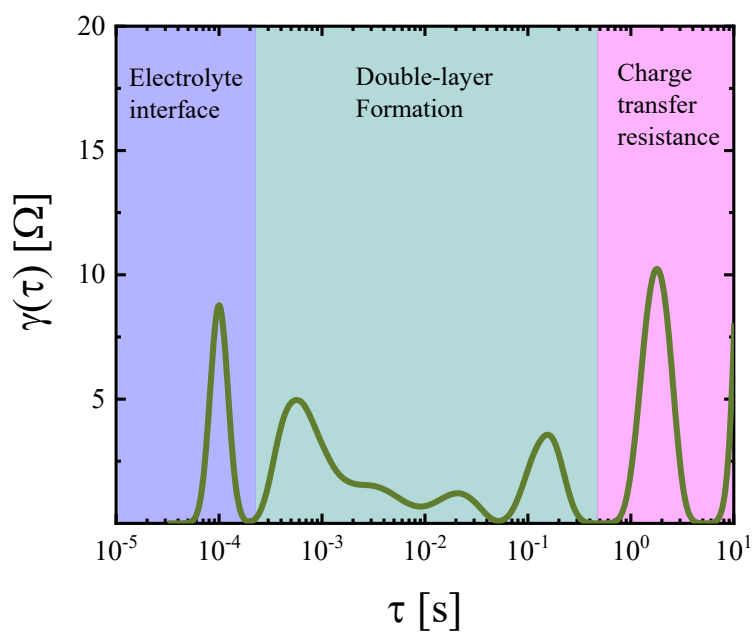


Figure 93 DRT calculation for the asymmetric coin cell assembled using recycled porous carbon.

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Curriculum Vitae

Curriculum Vitae

SECTION 1. PERSONAL INFORMATION

Name	URSINO FEDERICO
Address	40, VIA G. MOTTA 42, 95037, SAN GIOVANNI LA PUNTA (CT), ITALIA
Celluar	+39 3492581662
E-mail	federico.ursino@dfa.unict.it
E-mail alternativa	ursino.federico99@gmail.com
Nationality	Italiana
Place and date of birth	CATANIA, 14 GENNAIO 1999
Web page	https://www.dfa.unict.it/dottorandi/federico.ursino

WORK EXPERIENCE

Date	From 3-11-2025 to present
Employer	Università degli Studi di Catania – Dipartimento di Fisica e Astronomia “Ettore Majorana”
Employment	Research Fellowship
Duty	Scientific research and research project
Date	From 25-01-2022 to present
Employer	Scientific and Ecologic Minds Union
Employment	Founder and President
Duty	Contacts with public and private entities, logistics management of cultural and educational events

Curriculum Vitae

Date	From 01-08-2020 to 31-1-2021
Employer	Ontario s.r.l.
Employment	Occasional service contract
Duty	IT Technician for COVID-19 Patient Data Management at the Catania Health Authority

EDUCATION

Date	2022-2025
Istitution	Università di Catania, PhD on Material Science and Nanotechnology
Qualification obtained	PhD in Materials Science and Nanotechnology (expected graduation date: January 28, 2026)
Date	2020-2022
Istitution	Università di Catania, Dipartimento di Fisica e Astronomia “Ettore Majorana”
Qualification obtained	Master Degree in Physics (14/07/2022 with 110/110 cum laude)
Main topics	Condensed matter physics and Spectroscopy
Date	2017-2020
Istitution	Università di Catania, Dipartimento di Fisica e Astronomia “Ettore Majorana”
Qualification obtained	Bachelor degree in Physics (10/10/2020 with 106/110)

Curriculum Vitae

SPECIAL ASSIGNMENTS

Date	2022-2025
Research body	Consiglio Nazionale delle Ricerche – Istituto IMM (Istituto per la Microelettronica e Microsistemi), U.O.S. Catania (Università)
Role	Research Association
Main duties	Research in the field of Physics of Matter To participate in the research topic “Synthesis of nanostructured materials from industrial waste for electrodes useful for energy storage”, with reference to Project No. DFM.AD003.482 (SONICA - Sensoristica, energetica e fotonica).
Date	2018-2023
Research body	Università degli Studi di Catania
Role	Student Representative on the Department Council at the Department of Physics and Astronomy "Ettore Majorana"
Main duties	The Board regulates and defines the functioning of the aforementioned Department
Date	2021-2023
Research body	Università degli Studi di Catania
Role	Student Representative on the Council of the Master's Degree in Physics at the Department of Physics and Astronomy "Ettore Majorana"
Main duties	The Board regulates and defines the functioning of the aforementioned Council

Curriculum Vitae

Date	2018-2021
Research body	Università degli Studi di Catania
Role	Student Representative on the Council of the Undergraduate Degree in Physics at the Department of Physics and Astronomy "Ettore Majorana"
Main duties	The Board regulates and defines the functioning of the aforementioned Council

Date	2020-2022
Research body	Università degli Studi di Catania
Role	Student Representative at the University Internationalization Commission
Main duties	The College defines the internationalization policies of students at various levels for the entire university.

SECTION 2. TEACHING ACTIVITY

TUTORING FOR STUDENTS AT THE UNIVERSITY OF CATANIA

Period	Time	Course
AA 2023/ 2024	20 h	Tutoring activities in the "Physics and Applications of Physics" course in the Geological Sciences degree program (Prof. E. Bruno)
AA 2021/ 2022	20 h	Tutoring for all three-year degree courses at the Department of Agriculture, Food and Environment for the Physics courses (Prof. E. Bruno, Prof. L. Rapisarda, Prof. D. Lo Presti)

Curriculum Vitae

TUTORING FOR STUDENTS AT THE UNIVERSITY OF CATANIA

Period	Time	Course
AA 2023/2 024	20 h	Physics and Electrochemistry Laboratory in State High School “Ettore Majorana” San Giovanni La Punta (Catania), Italy

SECTION 3. RESEARCH ACTIVITY

After a summary of the research activity, this section is divided into 8 subsections, as follows:

- 3.a) PARTECIPATION IN ORGANIZING COMMITTEES
- 3.b) AWARDS AND RECOGNITIONS
- 3.c) CONFERENCE PRESENTATION, WORKSHOP AND SUMMER SCHOOL
- 3.d) PUBLICATIONS

RESEARCH ACTIVITY TOPIC

My research activity has focused on the synthesis of nanostructures obtained from industrial waste, using a low-cost hydrothermal process that is easily scalable to industrial levels. Subsequently, I devoted my work to their characterization, both from a structural and morphological standpoint — highlighting the presence of phases such as MoO_3 and MoS_2 — and from an electrochemical perspective, monitoring their performance in different environments and operating conditions.

My scientific interests also include Raman spectroscopy, particularly when applied in operando and coupled with electrochemical techniques such as cyclic voltammetry, galvanostatic charge–discharge, and electrochemical impedance spectroscopy (EIS).

Curriculum Vitae

The possibility of combining circular economy approaches with electrochemical measurements is gaining increasing attention within the scientific community, as demonstrated by the interest shown at the various conferences I have been fortunate to attend.

3.A) PARTECIPATION IN ORGANIZING COMMITTEES

- 2025 Organizing Committee Member Summer School “Materials for Energy and Sustainability X-International School of Materials for Sustainable Development and Energy”, Erice, Italia
- 2024 Organizing Committee Member Summer School "NanoSoLI2024", Erice, Italia.
- 2023 Organizing Committee Member Summer School “Materials for Energy and Sustainability X-International School of Materials for Sustainable Development and Energy”, Erice, Italia

3.B) AWARDS AND RECOGNITIONS

- 07/07/2025 **PhD Contest "Accenti le idee"**, The prize and the corresponding grant were awarded by the coordination council of the PhD program.
- 01/09/2025 **Translational access ReMade@ARI Project (PID: 34917)**, to perform: X-Ray Spectroscopy at ALBA, Barcelona, Spain; Electron Microscopy at ICN2, Barcelona, Spain; Laser Photochemistry & Spectroscopy at LLAMS, Amsterdam, Netherlands
- 04/04/2025 **Travel Grant ECS 2025**, The grant was awarded by the Electrochemical Society's Battery Division.

Curriculum Vitae

3.C) CONFERENCE PRESENTATION, WORKSHOP AND SUMMER SCHOOL

- Oral presentation titled “Low-cost processing of Mo recycled industrial powder into nanocatalysts for Oxygen Evolution Reaction and Hydrogen Evolution Reaction” at **ECS Meeting 2025**, Montreal, Canada, 18th-22th May, 2025
- Oral presentation titled “Facile synthesis of nanostructured MoS₂-nanoflakes by recycled industrial waste for energy applications” at **ECS Meeting 2025**, Montreal, Canada, Maggio 18th-22th May, 2025
- Flash presentation titled “Low-cost synthesis of nanostructured catalysts active for energy applications starting from industrial waste” at **SpecSchool2024**, Jesolo Lido (VE), Italy, 15th-20th September, 2024
- Oral presentation titled “Low-cost processing of Molybdenum industrial waste powder to obtain nanostructured catalysts for Oxygen Evolution Reaction and Hydrogen Evolution Reaction” at **EMRS 2024 Spring Meeting**, Strasbourg, France, 27h-31th May, 2024
- Oral presentation titled “Low-cost synthesis of MoO₃ and MoO₃/MoS₂ nanostructures from recycled waste for water splitting applications” at **EMRS 2023 Spring Meeting**, Strasbourg, France, 29th May- 2nd June , 2023

POSTER CONTRIBUTIONS

- o Poster presentation “Ammonium-ion storage in MoS₂-nanosheets synthesized from recycled industrial waste” at “**Materials for Energy and Sustainability X-International School of Materials for Sustainable Development and Energy**”, Erice, Italy, 8th-14th July, 2025

Curriculum Vitae

- o Poster presentation “Processing of molybdenum industrial waste into sustainable and efficient nanocatalysts for water electrolysis reactions” **at EMRS 2024 Spring Meeting**, Strasbourg, France, 26th-30th May, 2025
- o Poster presentation “Ammonium-ion storage in MoS₂-nanosheets synthesized from recycled industrial waste” **at EMRS 2024 Spring Meeting**, Strasbourg, France, 26th-30th May, 2025
- o Poster presentation titled “MoO₃-nanobelts active for energy applications synthesized starting from industrial waste” **at ECS Meeting 2025**, Montreal, Canada, 18th-22th May, 2025
- o Poster presentation titled “Hydrothermal growth of MoS₂/MoO₃ nanostructures from industrial waste powder for energy storage application” **at EMRS 2024 Spring Meeting**, Strasbourg, France, 27h-31th May, 2024
- o Poster presentation titled “Facile synthesis of sulfurized MoO₃ nanostructures from industrial waste powder for energy storage application” **at ICRC 2024**, Fraunhofer IWKS, Alzenau, Germany, 11th-13th March, 2024
- o Poster presentation titled “Low-cost synthesis of nanostructured catalysts for Oxygen Evolution Reaction and Hydrogen Evolution Reaction from Molybdenum industrial waste powder” **at ICRC 2024**, Fraunhofer IWKS, Alzenau, Germany, 11th-13th March, 2024
- o Poster presentation “Low-cost synthesis of MoO₃ and MoO₃/MoS₂ nanostructures from recycled waste for water splitting applications” **at “Materials for Energy and Sustainability X-International School of Materials for Sustainable Development and Energy”**, Erice, Italy, 3th-8th July, 2023
- o Poster presentation “Asymmetric supercapacitor device based on tungsten trioxide (WO₃) for Electrochemical Energy Storage” **at Workshop on Supercapacitor and Energy Storage**, Bologna, Italy, 19th-20th April, 2023

Curriculum Vitae

3.D) PUBLICATIONS

- Di Mauro; F. Ursino; G. Mineo; A. Terrasi; S. Mirabella MoO₃ Nanobelts Synthesized from Recycled Industrial Powder and Applied as Electrodes for Energy Storage Applications. *Nanomaterials* 2025, 15, 1380, <https://doi.org/10.3390/nano15171380>
- Ursino, F., Mineo, G., Scandurra, A. et al. Processing of molybdenum industrial waste into sustainable and efficient nanocatalysts for water electrolysis reactions. *Nano Res.* 17, 9585–9593 (2024). <https://doi.org/10.1007/s12274-024-6972-z>
- G. Mineo, F. Ursino, A. Terrasi, E. Bruno, S. Mirabella, Facile preparation of a highly efficient coin cell supercapacitor based on WO₃ nanorods, *Sustainable Materials and Technologies*, Volume 41, 2024, e01097, ISSN 2214-9937, <https://doi.org/10.1016/j.susmat.2024.e01097>
- G. Pellegrino, G., V. Strano, G. Marcellino, L. Pulvirenti, F. Ursino, S. Mirabella, G. G. Condorelli, Highly efficient - Bi₂O₃/Bi battery electrodes by reactive annealing from sol-gel precursors, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Volume 705, Part 2, 2025, 135738, ISSN 0927-7757, <https://doi.org/10.1016/j.colsurfa.2024.135738>.

SECTION 4. THIRD MISSION ACTIVITIES AND SCIENTIFIC OUTREACH

This section is divided into three main subsections, as listed below. The first concerns events organized on an annual basis, the second concerns specific outreach events, and the third concerns other activities promoting scientific culture:

- 4.a) CONTINUOUS ACTIVITIES
- 4.b) SPECIFIC EVENTS
- 4.c) OTHER ACTIVITIES

Curriculum Vitae

4.a) CONTINUOUS ACTIVITIES

Period	Event	Employment	Organizing body	Details
2024- PRESE NT	FAMELAB – il talent- show della Scienza, selezione di Catania (http://www.famelab-italy.it/)	Organizing committee	Università di Catania	As a member of the Scientific and Ecologic Minds Union I am participating in the organization of this event.
2024- PRESE NT	NanoBreak &Lab	Organizing committee	Department of Physics and Astronomy “Ettore Majorana”	I handle the event's graphics and promotion, especially among undergraduate and graduate students.

Curriculum Vitae

4.b) SPECIFIC EVENTS

Period	Event	Employment	Organizing body	Details
2025	NanoBreak & Lab	Speaker	Department of Physics and Astronomy “Ettore Majorana”	I presented the research work carried out during my PhD.
2025	Ambiente e Innovazione	Organizing committee	Città della Scienza e Scientific and Ecologic Minds Union	An event promoting scientific culture, aimed at demonstrating the connection between research carried out within UniCt and its positive impact on the local area.
2024	Sharper Night	Organizing committee	Università di Catania	Event to promote scientific culture
2023	FAMELAB – il talent-show della Scienza, Catania (http://www.famelab-italy.it/)	Competitor	Università di Catania	By passing the selection in Catania I gained access to the national contest, where I won the public prize.

Curriculum Vitae

4.c) OTHER ACTIVITIES

Period	Event	Employment	Organizing body	Details
2025	StartCup 2025	Competitor	Università di Catania and PNI	I presented a startup idea, called Accura, based on the scientific background I acquired during my doctorate. I won the third prize in cash for establishing the startup and access to the regional and then national phases of the competition.