





THESIS WORK FOR DUAL MASTER'S DEGREEITBAMag. in Energy and EnvironmentKITM.Sc. in Mechanical Engineering

DEVELOPMENT OF THE PROCESSING STEP FROM MOF TO SUPPORTED CATALYST BY ELECTROSPINNING

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Declaration by author

I, Macarena Alvarez, hereby declare that I have written this thesis independently and without external help. Only the sources explicitly stated in the thesis have been used. I assure that all texts in which the ideas of others have been taken over, either literally or in essence, have been marked as such.

Macarena Alvarez Karlsruhe, March 2022

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Abstract

In order to increase the flexibility of renewable energies and improve their integration into existing energy grids, efficient intermediate storage is necessary. High-purity hydrogen produced in a water electrolysis cell is a suitable energy carrier. However, the use of some electrolyzers is associated with high costs due to the required use of precious metals as catalysts, while others have disadvantages in terms of load modulation. In this sense anion exchange membrane water electrolysis (AEMWE) arises as an attractive alternative technology that combines convenient features of other type of electrolyzers. Nevertheless, there is a necessity in improvement regarding the performance of AEMWE. The oxygen evolution reaction (OER) in the anode, is the major source of energy loss and therefore, there is potential to optimize OER catalysts.

In this work, supported catalysts for the OER were developed using Metal-Organic Frameworks (MOF74) dopped with Ni and/or Co and fibers obtained from an electrospinning process, as supporting material.

The MOFs were pyrolyzed to obtain a carbon scaffold with finely dispersed transition metals, as well as the polymer fibers, which structure the catalyst, allowing to tune conductivity and mass transport.

Two different routes for combining the MOFs with the fibers were studied.

In order to investigate the electrospinning process, polymer concentration, solvent, applied voltage and polymer were varied. The improved parameters were selected and Polyacrylonitrile (PAN) fibers were successfully electrospun and pyrolyzed.

The MOFs were characterized physically, chemically and electrochemically. Pure Ni-MOF74 showed increasing current along the Cyclic Voltammetry cycles, reaching a mass-specific current of 732 mA mg⁻¹ after 50 cycles.

A supported catalyst was obtained after impregnation of the Ni-MOF74 over the pyrolyzed fibers and characterized. The combined catalyst showed a similar behavior compared with the pure Ni-MOF74.

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1 Introduction

For many decades there has been a major dependency on fossil fuels as a source of primary energy and as an energy carrier. However, there is limited amount of fossil fuel reserves to fulfill the ever-growing world consumption. In addition and not less important, greenhouse gas (GHG) emissions produced from fossil fuel combustion present a serious and increasing global environmental problem [1]. As a consequence of the increased GHG presence in the atmosphere, the global average temperature is estimated to increase by more than 3°C by 2050, which will cause unavoidable climate change and have considerable economic and social impacts [2]. In order to mitigate the effects of GHG emissions, research in developing technologies that utilize alternative and carbon-free energy resources has been intensified in the last decades.

One promising replacement for fossil fuels as energy carrier is the hydrogen. It is the most abundant energy carrier, and also present appealing characteristics as it is non-toxic, has a high mass energy density (39.4 kWh kg⁻¹) [3], and high energy efficiency (>70%) [4]. However, the majority of hydrogen produced commercially comes from industrial steam reforming processes. This processes that involve natural gases still emits a significant amount of CO_2 . Therefore other alternative technologies have been investigated to facilitate carbon-free production of hydrogen on an industrial scale such as thermolysis, photocatalysis, biomass gasification, and electrolysis [5].

Of these technologies, electrochemical water splitting employing renewable power sources is considered as a particularly feasible technology for the production of carbon-free hydrogen [4]. In this technology, a conventional electrolyzer uses a porous diaphragm that separates the anode and cathode in an alkaline solution [4,6]. The diaphragm conducts ions whilst also separating the produced hydrogen and oxygen into different chambers. This water electrolyzers based on liquid electrolytes are already being used commercially to produce highly purified and pressurized hydrogen [7]. Research on electrolyzer technology, however, has been focused on developing a system based on a solid polymer electrolyte membrane [7]. An electrolyzer based on a solid polymer electrolyte membrane consists of a membrane electrode assembly (MEA), with electrodes located on both sides of the electrolyte membrane [5].

This type of electrolyzers provide several advantages, compared to porous diaphragm electrolyzers, including improved operational efficiency and safety and simple gas separation [8].

The polymer electrolyte membrane based electrolysis systems are classified into proton exchange membrane water electrolysis (PEMWE) and anion exchange membrane water electrolysis (AEMWE). This is based on the types of ions conducted through the polymer membrane.

PEMWE exhibits greater hydrogen production energy efficiency compared to AEMWE owing to the high conductivity of the employed electrolyte membrane [9]. However, PEMWE requires the use of expensive and scarce noble catalysts such as iridium and ruthenium oxides. This is due to the fact that the catalysis of the oxygen evolution reaction (OER) occurs in corrosive acid electrolytes [10]

On the other hand, AEMWE works under alkaline conditions that allows non-noble metal oxides such as cobalt and nickel derivatives to be used as the water oxidation catalyst. This occurs as a result of their favorable OER activities in basic solutions.

This possibility represents a great advantage of AEMWE compared to PEMWE and can significantly reduce the associated costs since Ni or Co are substantially cheaper than Ir and Co [6]. However, the operation current density is higher in PEMWE. Comparing this two technologies in terms of operational current density, at the same working conditions (50°C, IrO₂ as the OER catalyst), showed that the density reported for AEMWE (approximately 0.5 A cm⁻² at 1.8 V) [11] is considerably lower than that reported for PEMWE (0.9 A cm⁻² at 1.8 V) [12]

Therefore, there is a necessity in improvement regarding the performance of AEMWE in order to be comparable with PEMWE.

To improve the cell performance of AEMWE, investigation of water electrolysis catalysts with higher activity should be done. The oxygen evolution reaction (OER) in the anode is a bottleneck for water splitting efficiency due to the sluggish kinetics of the 4 e⁻ transfer [13]. Therefore, this work proposes to investigate and characterize materials to be used as an OER catalyst and analyze the steps involved in its synthesis.

For this purpose, metal–organic frameworks (MOFs) were selected as part of the catalyst. The MOFs are crystalline materials that are composed of metal ions connected by organic linkers with a periodic, nano scaled structure and ultrahigh surface areas. They present tunable pore, flexible structure, and large surface-to-volume ratio. Due to this MOFs have a large potential in catalysis process [14].

Currently, intensive efforts are focusing on the structuring of MOFs at a bigger scale to use them as coatings, membranes [14], but the main problem is the intrinsic fragility of MOFs. This is related to the inorganic/organic hybrid character, resulting in a limited thermal and mechanical stability.

Alternatively, a more effective way to structure MOFs is the combination with polymer materials. The polymer which acts as a binder improves the mechanical flexibility and ensures chemical stability. Nevertheless, the integration of MOFs into a polymer matrix can result in poor MOF-polymer dispersion and compatibility issues.

One technic that shows a possible solution to this integration is the electrospinning. The electrospinning is a fabrication method to produce continuous ultrafine fibers with diameters in the range of a few tens of nanometers/micrometers in the form of nonwoven mats, yarns, etc. The mechanism is based on the ejection and elongation of a viscous polymer melt or solution under a high-voltage electric field which is then solidified in the electrified fluid jet on a collector [14].

As a precedent, electrospinning has recently been reported as an elegant approach for shaping various MOFs into hybrid materials with multiscale porosity and additional functionalities [14]. Also, the highly open and interconnected nanofiber structure showed excellent access of fluids that are appealing to catalysis. This way the polymer matrix allows the shaping but could also improves the handling, deployment, and regeneration of the composite material. This unique combination of properties makes porous MOF nanofiber structures a promising solution for OER catalyst.

In this work several MOFs candidates for OER catalyst and different polymers were combined through electrospinning technique. Afterwards the performance of these combinations, in order to finally be used as catalyst in AEMWE, was tested.

2 Theoretical background

In this chapter theory behind electrolysis principles is presented. In addition, some important aspects involved in the experimental process are overviewed, such as electrospinning basics, metal organic frameworks compounds characteristics (MOFs) and calcination principles.

2.1 Water Electrolysis

2.1.1 Electrochemical general basics

The process by which an electric current from an external source produces an oxidation-reduction chemical reaction in a chemical cell is called electrolysis. Basically, the electrolysis is the reversal of the processes in a fuel cell. Electrolysis thus converts electrical energy into chemical energy, resulting in the production of new compounds.

The already mentioned oxidation-reduction chemical reactions take place at the electrodes. At the anode, chemical species are oxidized by donating electrons, while at the cathode, chemical species are reduced by accepting electrons. In an electrolyzer, the electrons at the anode migrate to the cathode through an external circuit and this flux is promoted by an external power supply. At the same time, charge equalization takes place within the cell via ion transport through the membrane.

The cell voltage can be determined from the difference in the standard E_{00} reaction potentials in the two electrodes. These values are compared against the standard hydrogen electrode (SHE) [15]. Taking into account dependencies such as concentration, pressure and temperature, the electrode potential results from E_0 the Nernst equation [16]:

$$E_0 = E_{00} + \frac{RT}{zF} \ln\left(\frac{a_{0x}}{a_{Red}}\right) \tag{1}$$

Where R is the universal gas constant, a represents the activity of the oxidized or reduced chemical species. In the case of gases, the activity results from the partial pressure of the respective component. In the case of ions, the concentration corresponds to the activity.

Therefore, the equilibrium cell voltage U_0 results from the difference of the electrode potentials:

$$U_0 = \Delta E = E_0(Cathode) - E_0(Anode)$$
⁽²⁾

In the case of water electrolysis, the following equation corresponds to the overall reaction:

$$2 H_2 O(l) \rightarrow 2 H_2(g) + O_2(g)$$
 (3)

In Figure 1 a scheme of a water electrolytic cell is shown.



Figure 1: Schematic structure of an alkaline electrolytic cell [17].

As it was introduced before, electrolysis takes place in a vessel filled with conductive electrolyte. This electrolyte could be acid or alkaline. Depending on this the ions that are transported in the solution are H^+ in the case of acid electrolytes and OH^- in the alkaline ones.

Immersed in this vessel are the anode (+) and the cathode (-) where the oxidation and reduction reactions occur respectively.

These cells are operated with direct current. The electrolysis can be divided into two partial reactions taking place in each electrode.

On the cathode, the *hydrogen evolution reaction* (**HER**) takes place. The HER can be formulated as shown in equation (4).

$$4 H_2 O_{(l)} + 4 e^- \to 2 H_{2(g)} + 4 O H^-_{(aq)} \tag{4}$$

The left side shows the oxygen evolution reaction (OER), which proceeds as shown inequation (5).

$$40H^{-}(aq) \to O_{2}(g) + 2H_{2}O(l) + 4e^{-}$$
⁽⁵⁾

Regarding the potentials of the partial reactions is $E_{0,OER} = +0.401$ (V vs. SHE) and $E_{0,HER} = -0.829$ (V vs. SHE). Thus, for alkaline water electrolysis to occur, a minimum voltage is required (reversible voltage, Urev), which, according to the semi reactions potential (E_0) from Equations (1) and (2), is equal to 1.23 V ($E_{0,OER} - E_{0,HER}$) at standard conditions (1 bar and 25 °C) [17].

However, the real cell voltage (U) is always higher than the latter because of irreversibilities or overpotentials. Therefore, the real cell voltage can be defined as the sum of reversible voltage (U_{rev}) and the overpotentials (η), as shown in Equation (6):

$$U = U_{rev} + \sum \eta \tag{6}$$

The term $\sum \eta$ is the sum of activation, ohmic, and concentration overpotentials. These overpotentials are defined as follows [6]:

(1) Activation overpotentials: related to activation energies of hydrogen and oxygen formation reactions on the surface of electrodes.

(2) Ohmic overpotentials: sum of the electrical resistance of several components such as electrodes, current collectors, etc., and the transport resistance related to gas bubbles, ionic transfer in the electrolyte

(3) Concentration overpotentials: due to mass-transport limitations occurring on the surface of the electrodes at high currents.

The total contribution of these overpotentials to the cell voltage (U) can be analyzed through the polarization curve of an electrolysis cell, as represented in Figure 2.



Figure 2: Graphical representation of a polarization curve with the contribution of each overpotential [17].

The power density P is used to assess the efficiency of electrolysis and results from the product of current density and voltage. This is that at a given cell voltage a higher current density means a higher efficiency [15]. This higher efficiency is thus related to lower resistance.

2.1.2 Technologies: Alkaline electrolysis

There are several existing technologies to electrolyze water as shown in Figure 3 [18].

Among these technologies a technology already in the market is the Proton Exchange Membrane (PEM) type, where proton is the transport ion. This technology has good performance since it achieves significantly higher current densities [19]. compared to other technologies like Alkaline Electrolyzers (AE) as could be seen in Figure 4, that leads to higher production rates and more compact systems. As a negative side, to achieve this high loadings rare and expensive metals for catalysts and expensive corrosion resistant components are required (for example, bipolar plates based on high-quality Ti).



Figure 3: Water splitting electrolysis technologies for hydrogen production [18].



Figure 4: Comparison between alkaline, polymer electrolyzer membrane (PEM), and solid oxide electrolyzers in terms of voltage vs. current density [19].

As an alternative to these expensive components, the AE presents as a mature technology for H_2 production up to the MW scale and represents the most widely used electrolytic technology on a commercial level worldwide.

In this type of electrolyzes the most used anode and cathode materials are low-cost nickel or nickel alloy-plated steel materials [20], but AE has challenges as the handling of the corrosive electrolyte (alkaline media, like concentrated KOH solution) and limited current densities due to moderate OH^- mobility. Furthermore, the diaphragm in between the two electrodes does not completely prevent the cross-over of gases from one half-cell to the other and this reduces the efficiency of the electrolyzer, since oxygen reacts with the hydrogen present on the cathode side to form water. Additionally, extensive mixing (particularly hydrogen diffusion to the O₂ evolution half-cell) also occurs and must be avoided for safety aspects [20].

Trying to keep the best aspects of the PEM and AE, the Alkaline Exchange Membrane (AEM) was designed. Basically, this technology aims to combining the advantages of PEM (membrane separation, pure water feed) with the advantages of AE (cheaper and abundant materials for catalyser and an inexpensive nickel-based stack components [21,22].

AEM electrolyzers work with an alkaline environment at the membrane interface provided by the immobilized positively charged functional groups on the polymer backbone or on pendant polymeric side chains.

However, current AEM electrolyzers still need to be improved in terms of ionic conductivity, power efficiency, medium range membrane stability, the Ohmic resistance loss and catalyst loading [23].

Therefore, there is growing interest in developing a solid polymer anion exchange membrane, but more efforts are required regarding the catalyst design and synthesis.



A schematic and the overall cell reaction for AEM electrolysis are shown in Figure 5.

Figure 5: Single-cell components in AEM water electrolysis [24].

One aspect that shows the difference between these technologies is the efficiency. The efficiency for electrolyzers is defined in terms of the hydrogen produced per unit of electricity used to drive the electrochemical reaction. This efficiency would be 100% if all the electrons transported to the electrode conducted an effective electrochemical reaction [25]. The highest efficiency is shown by PEM performing between 70 and 90%; followed by AE with an efficiency between 60 and 80%. The smallest efficiency range is shown by AEM that is between 50 and 70%.

Another point to be compared is the purity of the hydrogen that is obtained. While in PEM a high purity of up to 99.9995% could be obtained, in the case of AE this value amounts to only 99.5%. In this aspect AEM represents an improvement over AE with a purity of 99.9% [25].

Regarding the operating conditions, AE works at lower pressures than PEM, the first ones between 1-30 bar, compared to the range of 50-80 bar of the second ones. In the case of AEM they work in the same range as AE. Regarding the working temperature, AE and PEM have similar working ranges, 60-80 °C and 50-80 °C respectively, while AEM operates in a lower range between 50-60 °C [20].

These characteristics and some further comparisons are summarized in Table 1.

84. 	Alkaline	PEM	AEM
Electrolyte	Aqueous KOH (20–40 wt%)	Proton exchange ionomer (e.g. Nafion)	Anion exchange ionomer (e.g. AS-4) + optional dilute caustic solution
Cathode	Ni, Ni-Mo alloys	Pt, Pt-Pd	Ni and Ni alloys
Anode	Ni, Ni-Co alloys	RuO ₂ , IrO ₂	Ni, Fe, Co oxides
Half-cell separation	Diaphragm (Zirfon Perl 500 µm)	Nafion 117 (e.g. 180 µm)	AEM (20-100 µm)
Current density (A cm-2)	0.2-0.4	0.6-2.0	0.2-1.0
Cell voltage (V)	1.8-2.4	1.8-2.2	1.8-2.2
Cell area (m ²)	<4	<3	Lab testing cells
Operating temperature (°C)	60-80	50-80	50-60
Operating pressure (bar)	1-30	30-76	1-30
Production rate (Nm3 h-1)	<760	<40	<1
Gas purity (vol%)	>99.5	>99.9999	>99.99
System response	Seconds	Milliseconds	na
Stack lifetime (h)	60k to 100k	20-60k	na
Technology status	Mature	Commercial	R&D

Table 1: Comparison of the main characteristics of alkaline, PEM and AEM water electrolysis [20].

2.2 Metal Organic Frameworks (MOFs)

Metal–organic frameworks (MOFs) are a group of compounds consisting of metal ions or clusters coordinated to organic ligands to form one-, two-, or three-dimensional structures.

MOF-74 are a family of MOF constructed by the coordination of divalent transition metals and 2,5dioxidoterephthalate with a formula of $M_2(DOT)(H2O)_2$ (M = Mg, Mn, Fe, Co, Ni, and Zn; DOT = 2,5-dihydroxyterephthalate) [26].

The synthesis of MOF-74 can be carried out under mild reaction conditions and the use of harmful reagents and solvents can be avoided. After the synthesis, the MOF-74 could be "activated" by the extraction of the solvents absorbed by the structure, by a controlled vaccum process.

In Figure 6 is showed a scheme of the synthesis and the obtained MOF-74, with MG as the divalent metal, as an example.



Figure 6: Single crystal structure of Mg-MOF-74, formed by reaction of the DOT linker with Mg(NO3)2-6H2O. C atoms are shown in gray, O atoms in red, 6-coordinate Mg atoms a and terminal ligands in pink, and 5-coordinate Mg atoms in blue. H atoms and terminal ligands on the fragment at top right are omitted for clarity [27].

The following figure provides a clearer view of the metal sites (in this case, with a Ni-MOF-74 as the example).



Figure 7: Representation of the fully desolvated Ni(dhtp) structure showing the hexagonal 1D channels (upper picture: view towards the (113) plane, lower picture: view towards the (120) plane) [28].

Some possible applications of MOFs, that received considerable attention over the past decade, are in the field of gas purification and storage as well as catalysis and drug delivery [29].

An interesting characteristic features of MOF-74 is the composition of the divalent metals nodes (M = Mg, Mn, Fe, Co, Ni, Zn, etc.) that can be widely selected and modified [30].

Through controlled thermal treatment, mixed metals could be sequentially degraded from MOF substrate to obtain highly active heteroparticles which are difficult to construct by conventional methods. These features make MOF-74 an ideal precursor to synthesize composite catalysts with extensively tunable properties. [26] This is due to the fact that an efficient electrocatalyst for OER should offer fast mass transport and accessible active sites of its own.

One strategy to achieve this challenging goal is to prepare a MOFs and then pyrolyze it to obtain a carbon support with homogeneously distributed metal sites.

The periodic arrangement of metal nodes and organic linkers in MOF structure leads to a homogeneous distribution of metal oxide nanoparticles and in situ formed carbon supports [31].

Therefore MOF-74 was chosen as the optimal material to be used as a precursor for the fabrication of electrocatalysts. In this work MOF-74 were synthesized, based on 2,5-dihydroxyterephthalic acid (DOT) and nickel and cobalt in different ratios, transition metals that showed good performance in OER [28].

In addition, the intrinsic fragility of MOFs needs to be considered which is related to the inorganic/organic hybrid character of this class of materials and the resulting limited thermal and mechanical stability. [32] Alternatively, a more effective way to structure MOFs is the combination with polymer materials. The polymer which acts as a binder improves the mechanical flexibility and ensures chemical stability [32].

2.3 Electrospinning

Electrospinning is a fabrication method to produce continuous ultrafine fibers with diameters in the range of a few tens of nanometers to a few micrometers in the form of nonwoven mats, yarns, etc. In this method, an electrostatic force produced by a high voltage supply is used to drive the spinning process. This field is applied to droplets of polymer solution (or a melt) passed from the tip of a fine orifice [33].

The mechanism of electrospinning is based on the ejection and elongation of a viscous polymer melt or solution under a high-voltage electric field which is then solidified on a collector [34]. When an electric field is applied to a liquid droplet, an electrostatic charge accumulates at the tip of this droplet. Therefore, charge repulsion works against the surface tension, causing the shape to change from a spherical surface to an elongated cone shape (called Taylor Cone). As the liquid contains a polymer as a solute, the polymer viscosity will oppose the breaking up of the jet into droplets and produce a thread of polymer solution.

As a result of the motion and stretching, solvent is removed, and the polymer thread elongated.

In the electrospinning process the fibers transport charge across the gap between the charged needle and the grounded collector plate, closing the circuit. As reported by Fong et al. [35], during the electrospinning process the electric current due to ionic conduction of charge in the polymer solution is so small that is considered negligible, so the only mechanism of charge transport is the flow of polymer from the tip to the collector plate [36].

The equipment needed for electrospinning on a laboratory scale is relatively simple; in the basic setup there are three main components: the high voltage power supply, a syringe pump and the collector. A schematic of the equipment used for electrospinning is shown in Figure 8.



Figure 8: Schematic of the equipment used for electrospinning [31].

In this setup, the fibers are deposited as a random mat. If it is the case that a random mat is not suitable, and an array of aligned fires is required [37] a rotating collector could be used [38].

2.3.1 Processing Parameters

There are many variable parameters that may affect the fiber properties, such as its diameter and morphology.

These parameters could be classified into three categories: (a) polymeric solution parameters (concentration, viscosity, surface tension, molecular weight, and solvent type), (b) operation parameters (voltage, solution flow rate, needle-collector distance, needle tip design, collector geometry, and velocity), and (c) the ambient parameters (humidity and temperature) [34,39,40].

2.3.1.1 Concentration

The viscosity of the polymer solution can be regulated by varying the concentration, and it is an important factor that affects the fiber morphology and diameter values. When a solid polymer is dissolved in a solvent, the solution viscosity is proportional to the polymer concentration. Thus, a higher polymer concentration gives a higher viscosity and a higher viscosity result in a larger fiber diameter [37].

The viscosity could be increased also by changing the molecular weight of the polymer in the solution [41].

It has been found that the polymer concentration also affects the formation of the beads. Fong [35] recognized that higher polymer concentration resulted in fewer beads. It should be realized that with the higher concentration reported the beads were not reported to completely disappear. Instead, the bead diameters, if any, at higher concentrations were even larger. The shape of the beads changed from spherical to spindle like when the polymer concentration varied from low to high levels.

Characterization of the formation of electrospun beaded nanofibers shows that solution viscosity, net charge density carried by the electrospinning jet and surface tension of the solution are the main factors. Higher viscosity favors formation of fibers without beads, higher net charge density not only favors formation of fibers without beads, but also favors the formation of thinner fibers. Surface tension drives towards the formation of beads, hence reduced surface tension favors the formation of fibers without beads [35].

Yang et al. [42] reported the same findings for low concentrations of polyvinylpyrrolidone (PVP) in solution producing the 'beads-on-a-string' morphology. At 20 wt % it was observed that the fibers formed a helical pattern on the collector, resulting from the bending instability of the process. The process was unsuccessful from 25 wt % as the viscosity of the solution was too high, meaning the surface tension had become too strong and prevented disruption of the Taylor cone. In addition, they found that further increase of concentration caused the average fiber diameter

to increase from 120 nm to 1.5 mm for concentrations of 2 wt% to 10 wt%. Gomes et al. [36] also reported an increase in the average diameter of fibers from 175 nm to 575 nm for concentrations of 4 wt% to 10 wt % of a precursor solution of polyacrylonitrile (PAN) in N,N dimethylformamide (DMF). The link between increasing the concentration of a solution and the resultant increase in fiber diameter could be explained as it follows. If there is more polymer in the Taylor cone at the point of disruption, there will be more polymer in the fiber jet and after drying a thicker fiber will be produced [34].

Though the viscosity supplies some control of the fiber parameters, other factors need to be considered. Surface tension may not contribute hugely to the tunability of the system in normal circumstances, but when the viscosity is low this will start to influence the fibers in terms of the beading [43]; conductivity increases the charge separation and increases elongation and thus it would seem an increase in conductivity will result in a decrease in fiber diameter [41].

2.3.1.2 Solvent

Electrospinning should be carried out in a suitable solvent. Though many of the crucial parameters (such as viscosity) depend on the properties of the polymer, the solvent is also important in the electrospinning process.

Particularly important factors are: the vapor pressure, which can have a major effect on polymer morphology; the polarity which will influence the conductivity and hence interaction with the electric field; and finally, the surface tension, which is a force to be overcome by the electric field [41].

Yang et al. [42] investigated the influence of solvent on electrospinning poly(vinyl pyrrolidone), showing that the morphology of the nanofibers electrospun from ethanol, dichloromethane (MC), and DMF strongly depends on the type of the solvents used. Nanofibers from ethanol were largely smooth, with a wide diameter distribution ranging from 100 to 625 nm while a lot of beads exist on the nanofibers from the DMF and MC solution. This formation could be attributed to the high surface tension and low viscosity of the PVP/DMF and PVP/MC solutions, whereas the PVP/ethanol solution possesses a lower tension and higher viscosity. They also investigated the effect of both mixed solvents, ethanol/MC and ethanol/DMF finding that the surface tension and solution viscosity could been adjusted by changing the mass ratio. They reported that the mixed solvent ethanol/DMF with a mass ratio of 50/50 was found to be a good solvent to produce thinner fibers with no beaded formation.

2.3.1.3 Voltage

Regarding the influence of the voltage applied in the fiber morphology Zhang et al. [44] observed that the fiber diameter of PVA nanofibers increased with the increase in high voltage and Gomes et al. [36] observed the same effect on PAN nanofibers. They also reported that applied voltage strongly affects the shape, length and morphology of the fibers. Other researchers like Yuan et

al. [45] claim that the higher voltages facilitate the formation of smaller fibers because of the increase in electrostatic repulsive forces, thus, more stretching.

2.3.1.4 Flow rate

The flow rate is also an important factor which affects the velocity of the jet and fiber diameter. In general, a lower flow rate is preferred to avoid beaded fibers as the solution gets enough time to dry with higher stretching forces on jet. Yuan et al. [45] investigated the morphological change on polysulfone (PSF) fibers with the change in flow rate and observed lower diameters at a lower flow rate

2.3.1.5 Collecting distance

The distance between the collector and the needle regulates the electric field intensity which in turn controls the fiber morphology. Increasing the distance will increase the time of flight, resulting in stretched and further elongated fibers [46]. Beads start to appear with a higher distance between the needle and the collector, but formation of beads could also be seen with lower distances as the time to solidify is not sufficient [47].

Lower distance avoids solvent drying, and fibers stick to each other [39]. The solvent drying phenomenon is an important aspect as it morphs the fiber geometry, so distance needs to be optimized. Yuan et al. [45] observed lower diameter values at larger distances.

Regarding the compared influence of the parameters in the fiber size and morphology, the concentration showed to be the most important factor. Also the election of the solvent proved to be a decisive factor [42].

Utkarsh et al. [39] studied the effects of five major parameters on the electrospinning of different PVP-ethanol solutions and the minimum fiber diameter was found to be controlled by two main design variables: polymer concentration and voltage applied, as both showed significant effects on the measured fiber morphology. On the other hand, the flow rate, and collecting distance had the least significant effects compared to the other two.

2.3.2 Materials

A lot of polymer-solvent systems have been used to produce nanofibers via electrospinning. The important features are the solubility or the ability to melt the polymer, and that the molecular weight is sufficiently high to allow entanglements between polymer chains [41].

Some examples are polystyrene (PS) in tetrahydrofurane (THF), polyvinylpyrrolidone (PVP) in ethanol (EtOH), and polyacrylonitrile (PAN) in dimethylformamide (DMF) [48].

Electrospinning has been used to prepare more complex systems than simple polymers

Inorganic materials can be produced by electrospinning; for example, a metal oxide/polymer mixture. In addition, composite fibers have been prepared, incorporating a range of particles for example, carbon nanotubes have been incorporated into poly(acrylonitrile) which on pyrolysis produce carbon fibers [34].

Combination of MOFs with the electrospinning

Another material that could be incorporated to the fibers are the MOFs. Electrospinning has recently been reported for shaping various MOFs into hybrid. MOF/polymer nanofibers with hierarchical porous structure combine the advantages of both types of materials, including structural flexibility, light weight, large surface area-to-volume ratio, high porosity, and tunable pore size at varied length scale [32].

Lai et al. [49] showed that the combination of a methanolic solution of PVP and ZIF-8 for electrospinning and posterior calcination enhanced the specific surface area and improved pore distribution compared with the same materials without electrospinning, to obtain an electrocatalyst for oxygen reduction. This will be beneficial for strengthening the mass transfer and increasing the use of active sites.

Two major routes have been developed for the structuring of MOF-polymer nanofiber architectures based on electrospinning, which are "direct electrospinning" and "surface decoration" [32]. In direct electrospinning, a mixture of a slurry that contains MOF particles and a polymer solution is directly electrospun into a composite nanofiber [50]. The resulting MOFs are embedded in a polymeric nanofiber matrix. The second structuring route is the growth of MOF particles on the surface of the nanofibers [32].

Polymers examples used in Electrospinning

PVP and its polylactide blends were first used for electrospinning to fabricate fibers in 2001 [51]. It has been widely used to manufacture fibers from different materials using the electrospinning process because of its spinability and fiber extraction. Several metal oxide filler materials like Titanium Oxide (TiO2) and Zinc Oxide (ZnO) were mixed with PVP to manufacture nanofibers using the electrospinning method. Also, conductive polymers, biopolymers, and other organic/inorganic compounds were used as a filler in the PVP polymer matrix and directly blended with the PVP solution to obtain PVP-based electrospun fibers. Studies on various solvents such as ethanol, water, N,N-dimethylformamide (DMF), and methanol have been reported to

investigate the potential of PVP nanofiber fabrication via the electrospinning process and its morphological variation [39] [51].

In Figure 9a the chemical structure of the PVP is showed.



Figure 9: Chemical structures of (a) PVP polymer and (b) PAN polymer [52].

PAN is recognized as the most important and promising precursor for carbon fiber. There are numerous advantages for PAN fibers, including high degree of molecular orientation, and higher melting point and thermal stability [52]. This polymer is also widely used in electrospinning [48] and combined with calcination for energy applications [53].

In Figure 9b the chemical structure of the PAN is showed.

Calcination/Pyrolysis

The pyrolysis process to make carbon fibers from PAN precursor include the steps of stabilization and posterior carbonization.

The PAN fiber is first stretched and simultaneously oxidized in a temperature range of 200–300 °C. This treatment converts thermoplastic PAN to a non-plastic cyclic or a ladder compound [54].

During the production of carbon fiber, one of the key processes is the stabilization process, during which PAN fibers are converted to infusible, nonflammable fibers [55]. During this process, complex chemical reactions occur, accompanied by significant enthalpy changes and thermal shrinkage. In an inert atmosphere, cyclization of the PAN molecular chains and the liberation of micromolecular gases take place. In air, the situation becomes much more complicated due to the presence of oxygen [55].

Xiao [55] illustrates the structural evolution of PAN during thermal stabilization in inert gas (Figure 10) and Konstantopoulos the carbonization mechanism on PAN fibers [56], also under N_2 (Figure 11).



Figure 10: Structural evolution of PAN during thermal stabilization in inert gas [55].



Figure 11: Carbonization mechanism of PAN fibers [56].

The cyclization is the only occurring action under N2 conditions, since dehydration, dehydrogenation and oxidation reactions are triggered by the presence of O₂. [56]

3 Analysis Methodology

3.1 Scanning Electron Microscopy (SEM)

The Scanning Electron Microscopy (SEM) is used for morphological characterization of the surface of solids. The main advantages of SEM are the high resolution (\approx 100 Å) and the large depth of field that gives a three-dimensional appearance to the images. It permits the observation and characterization of heterogeneous organic and inorganic materials on a nanometer (nm) to micrometer (µm) scale.

In this physical characterization method, the sample surface is bombarded with a beam of electrons (primary electrons). The interactions between the materials under investigation and the electrons are used to generate an image of the surface.

The primary electrons (PE) are generated by an electron gun that commonly consist of a tungsten wire filament serving as the cathode (negative electrode), the grid cap or Wehnelt (control electrode), and the anode (positive electrode). The wire is heated by an electric current to a temperature of 2000-2700 K. Thus, electrons are emitted from the tip and accelerated via an electric field generated between the hot cathode and the anode. The accelerating voltage is selected in the range between 0.1 to 30 kV [57]. The column in which the electrons are accelerated and focused, as well as the sample chamber, are subjected to a high vacuum (<10-4 Pa). Using a lens system and an aperture diaphragm, the PE are focused into a beam with a diameter of less than 10 nm.

By means of a deflector coil a selected portion of the sample surface is scanned with the electron beam, point by point in rows and columns.

The impact of the electron beam on the sample causes the emission of, among other things, secondary electrons (SE) and backscattered electrons (BSE).

Backscattered electrons are electrons from the principal electron beam that were elastically scattered by the positively charged atomic nuclei. Secondary electrons are electrons from the outer shells of the sample atoms that were released by the impact of the primary beam with the sample (inelastic scattering).

The BSE and SE are detected respectively. Information can be obtained from the properties of the detected electrons. While the low-energy SE are scattered from the near-surface regions, the higherenergy BSE originate from the deeper regions of the excited sample volume. As a result, pure surface features can be more clearly visualized using the SE, whereas the BSE produce an enhanced depth effect. The detected electrons are converted into electrical signals, which are then transferred into an image of the object surface using analysis software. The inclination of the hit surface elements to the recording surfaces of the detectors, as well as the direction of the reflected electrons have an influence on the brightness and the contrast effect during image formation [57].

In addition to the SE and RE, X-rays are produced in the sample and can be analyzed with an energy dispersive X-ray spectrometer (EDX). The X-rays are characteristic of the specific element from which they are emitted. Consequently, a spectrum of the elements (line profiles) can be formed from a qualitative analysis of the X-rays. After a qualitative assignment of the peaks has been made, a quantitative evaluation can be made via the signal intensity. The signal intensity is directly

proportional to the concentration of the respective element. Complementary to the line profiles, a distribution image can be generated showing the element distribution on a surface. Hydrogen and helium do not emit X-rays, so they cannot be detected by EDX [57].

The advantages of SEM include the selection of a large magnification range and a high depth of field. In addition, elemental distribution analysis can be performed with EDX coupling, allowing detection of unknown particles or inhomogeneities, for example. [57]

The measurements were performed by Hubert Weyrauch at the ICT. A SEM model ZEISS EVO MA 10 was used for the the measurements and a EDX from the Company Oxford Instruments, model X-Max SSD (silicon drift detector) detector, 50 mm².

3.2 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is a type of destructive testing, in which the change in mass of a sample is monitored as a function of temperature or time in a temperature and atmosphere-controlled environment. The principle of this type of analysis is to quantify the amount and rate of change of mass loss of the sample as the temperature increases. TGA allows characterization of materials that show weight loss or gain due to decomposition, oxidation and/or dehydration of the material in question.

The equipment used to perform this type of test consists of a precision balance on which is mounted a capsule of inert material (platinum or aluminum, depending on the selected temperature range) in which the sample is loaded. The balance, in turn, is inserted into an oven whose atmosphere is controlled by inert gas dragging, N₂ in this case. Likewise, the temperature is programmed to vary over time, according to a predefined increment. The equipment registers the weight on the balance at preset time intervals and transmits the information to a computer, with which graphs of the variation of the mass of the sample as a function of temperature, called thermograms, are assembled.

When one of the substances undergoes transformations due to the temperature increase, among other changes, it releases gases that are carried away by the stream of inert gas that assists the equipment, cleaning the atmosphere during the entire test. In the thermogram it is often difficult to locate the temperatures of the thermal events that occur, since the loss of mass is not always abrupt. Therefore, use is made of the curve of the first derivative of mass with respect to temperature as a function of temperature ($\partial M/\partial T$ vs T). The derivative of the curve resulting from the thermogravimetric analysis makes it possible to determine the inflection points (temperature corresponding to the maximum degradation rate) for each mass loss step (6). This curve is called DTG, which stands for derivative thermogravimetry.

The TGA of the polymer fibers was performed by the group of Bea Tübke at the ICT. An NETZSCH TG 209 F1 Iris[®] vacuum-tight thermobalance was used to test the polymer fibers. With this balance, investigations can be carried out in the temperature range between room temperature and 1000 °C with a resolution of 0.1 μ g. Two purge gas inlets and one inert gas are available for the analyses, which are precisely controlled by a mass flow controller integrated in the instrument. The data acquisition

as well as the control and evaluation of the measurements was realized with the Proteus software from Netzsch.

Approximately 10 mg of the sample was weighed into aluminum oxide crucibles and the measuring program (see Table 1 below) was started.

Parameter	Device setup
Temperature range	25 - 1000°C
Gas	Nitrogen
Heating rate	10 K/min
Gas flow rate	20 ml/min
Crucible	Al ₂ O ₃

Table 2: Working parameters on the TG

TGA of the MOFs were carried out on a TGA Q5000 TA Instruments device. The samples were heated under N_2 atmosphere at a heating rate of 10 K min⁻¹ up to 700 °C. The measurements were performed by the group of Dr. Piscopo at the ICT.

3.3 Inductively coupled plasma-optical emission spectroscopy

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) is a technique for the determination of the elemental content of a sample and its concentration. Optical emission spectroscopy (OES) is one of the analytical techniques based on Atomic spectrometry, for which one of the atomization/excitation sources could be inductively coupled plasma (ICP) [58]. With this technique, liquid samples are converted into an aerosol and injected into a radiofrequency (RF)-induced argon plasma [58]. The sample is desolvated, vaporized, atomized, and excited and/or ionized by the plasma. Once the atoms or ions are in their excited states, they can decay to lower states through thermal or radiative (emission) energy transitions. The intensity of the light emitted at specific wavelengths is measured and used to determine the concentrations of the elements of interest [58].

Solid samples cannot be introduced into the plasma directly therefore they must be either transferred into the plasma using a solid-sample accessory or they must be dissolved or digested into a solution [59]. The main techniques used to dissolve solids are acid digestion and fusion.

The digestion or extraction of soil samples can be performed with aqua regia, which is a solution composed of nitric and hydrochloric acid at a 1:3 ratio.

The measurements were performed by the group of Bea Tübke at the ICT. The machine used for the measurements was a ICP-OES Modell iCap 6300 from the company Thermo Scientific. The sample was digested in duplicate using microwave pressure digestion (KöWa) and the insoluble residue was then filtered off using white belt filters. The solvent used was aqua regia (6 ml hydrochlorid acid and 2 ml nitric acid).

3.4 Rotating Disk Electrode (RDE)

Basics

Cyclic voltammetry (CV) is an electrochemical method for the investigation of electrode surfaces and electrocatalysts. In this method, the potential of the working electrode E_{WE} is varied linearly between a lower potential and an upper potential by a potentiostat and the resulting current I is measured. The rate of change of the potential over time is called scan rate (v). This is typically between 1 and 1000 mV s⁻¹. This type of measurement, in which the potential is specified as constant and the resulting current I is measured.

A cyclic voltammetry experiment is carried out in an electrochemical cell with a so-called threeelectrode set up [60]. The three electrodes are a working electrode, a counter electrode, and reference electrode.

The reference electrode is needed since the potential E of an electrode in an electrochemical cell is not directly accessible and only potential differences can be measured.

If the potential of the reference electrode is known, the potential of the working electrode E_{WE} with respect to the reference electrode can be specified. In this project a reversible hydrogen electrode (RHE) is used as reference electrode. While the potential of the working electrode is changing, the current between the working electrode and the counter electrode flows [60]. The resulting graph is called a cyclic voltammogram. Depending on the conductivity of the electrolyte, a voltage drop occurs between the working electrode and the reference electrode, the so-called IR drop. This is usually determined by impedance spectroscopy and the potential of the working electrode is corrected accordingly.

The advantage of this electrode is that the potential of the RHE E_{RHE} adjusts to the pH.

The pH-dependent electrode potential of the RHE E_{RHE} can be calculated for 298 K as follows:

$$E_{\text{RHE vs. SHE}} = -59 \, mV * pH \tag{7}$$

The RHE is referred to the standard hydrogen electrode (SHE). The potential $E_{SHE} = 0$ is assigned to the SHE under standard conditions (T = 298 K, p = 0.1 MPa, pH = 0).
Preparation of the RDE

For the preparation of the Rotating Disk Electrode (RDE), a catalyst ink with a catalyst concentration of 1 mg mL-1 is first prepared. The five MOFs pyrolyzed and the supported MOF were tested as catalysts and therefore used to prepare the ink. Approximately 2 mg of each catalyst is weighed, grinded and dispersed in the appropriate amount of a 20 vol% 2-propanol / 0.02 wt% Nafion[™] water solution as a binder. The catalyst ink is homogenized in a Sonifier Branson 250 with an ultrasonic horn of 3 mm of diameter, two times with the following parameters: energy per pulse 12 J, time between pulse 0050 sec, total energy 2500 J and amplitude 25 %. The bottle containing the ink was inside a bath of ice/water during the homogenization to avoid the heating of the ink. The electrode used is a Pine Research Instrumentation RDE electrode with a glassy carbon (GC) disk for high temperature. The diameter of the disk is 2.5 mm. The RDE electrode is first polished on a polishing cloth with a 0.05 µm diamond suspension for 5 minutes. The electrode is then cleaned in an ultrasonic bath in ultrapure water (0.056 µS cm-1 at 25 °C) for 5 minutes. The RDE is fixed on a Pine Research MSR Rotator, with the electrode facing up, and an aliquot of 10 µL of the catalyst ink is added to the disk of the RDE using an Eppendorf pipette. This gives a catalyst loading showed in Table 3.

Catalyst	Loading Ni-Co electrode	
	[µg/cm²]	
Ni-MOF74	38.54	
Ni ₇₅ Co ₂₅ -MOF74	37.49	
Ni ₅₀ Co ₅₀ -MOF74	37.63	
Ni ₂₅ Co ₇₅ -MOF74	35.57	
Co-MOF74	30.09	
PAN+Ni-MOF74	23.76	

(The previous values were calculated with the result of the ICP-OES for the concentration of Ni-Co of the catalysts.)

The catalyst ink is dried for 40 min - 60 min at a rotation of 250 rpm. Photographs are taken under an optical microscope to check the homogeneity of the catalyst layer. Figure 12 shows a representative catalyst layer of some of the catalysts.



Figure 12: Photographs taken under an optical microscope of the catalyst layer . (a) Ni₇₅Co₂₅-MOF ; (b) Ni-MOF

Experimental Setup

The measurements for the investigation of the electrocatalyst are carried out in a three-electrode glass measuring cell with a volume of 150 mL with a potentiostat from the company BioLogic (model SP 300). The cell is filled with a 1 M KOH solution (analaR NORMAPUR - VWR) as electrolyte. A platinized Pt sheet is used as the counter electrode and a reversible hydrogen electrode (RHE) is used as the reference electrode. The reference electrode is added to the three-electrode measuring cell via an electrolyte bridge, which is also filled with a 1 M KOH solution.

A gas inlet with argon supply is used to purge and agitate the solution, which can be switched over via a 3-way stopcock depending on the measurement.

The three-electrode measuring cell has a jacket warming system, which is used to set the experimental temperature with a 17 wt% ethylene glycol-water mixture as the warming liquid via a thermostat. The measurements were performed at 26 °C. The three-electrode measuring cell is tempered for at least one hour before the measurements to set the appropriate experimental temperature. Figure 13 shows the experimental setup.



Figure 13: Experimental setup RDE measurements: Three-electrode measuring cell.

Measurements

OER measurements

Before performing the OER measurement, the Argon supply is turned on and a rotation of the RDE of 1600 rpm is set. This condition is maintained along all the measurements. Cyclic voltammetry

measurements are performed in a potential range between 1.2 V vs. RHE and 1.7 V vs. RHE with a potential sweep rate of 10 mV s⁻¹. This cycle is repeated 50 times.

At the end of the measurement series, the argon purge is switched off and the rotation is stopped.

To present the results, the measured current was divided by the mass of active material (Ni and Co) deposited over the electrode, obtaining a mass-specific current or "Mass activity".

Determination of the IR drop by impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is performed to determine the electrolyte and cell resistance used to calculate the IR drop. First, the argon supply is turned on and then the rotation speed of the RDE is set to 1600 rpm.

A sinusoidal AC voltage U(t) is specified as the excitation function. The starting point of the AC voltage is chosen to be 1.6 V vs. RHE since this potential is of interest in the measurements. The voltage is varied with an amplitude of 10 mV in a frequency spectrum ω of 1 MHz-1 Hz. The response function of the AC current I(t) is measured, as well as the impedance Z(ω) from it. The resistance could be obtained from the real part of the lowest point of the curve -Im(Z) vs Re(Z).

3.5 Brunauer-Emmett-Teller Gas Adsorption

Fundamentals

Gas physisorption is the commonly used technique to characterize porous materials. The method is based on the physisorption of gas molecules on the external and internal surface of the material. The adsorbate adsorbs to the material surface through reversible weak Van der Waals forces. Nitrogen, Argon, and Krypton are the commonly used gases for this method. The first two gases are used for porous materials with a high surface area.

Porosity could be classified into three different types according to their porous diameter (D): microporous (D<2nm), mesoporous (2nm<D<50nm), and macroporous (D>50nm) [61].

Brunauer-Emmett-Teller (BET) method

This is a method used to determine nanomaterial surface area and the most common one. The BET method was designed to directly measure the specific surface area and pore sizes of powdered samples under high-vacuum conditions [62].

In a typical BET analysis, nano material surface is determined from the volume of nitrogen (N_2) gas adsorbed by the material. N_2 gas is assumed to have access to the entire nano material surface. The surface area measurements are based on adsorption of gas molecules in infinite layers with no interlayer interaction. Under these conditions, the basic Langmuir theory can be applied to each layer to derive the BET surface area for nano materials (S_{BET}).

$$S_{BET} = \frac{V_0 N_a s}{M_v}$$

where, V_0 is the volume of single monolayer of adsorbed gas, N_a is Avogadro's number, M_v is molar volume of gas adsorbate and **s** is the surface area of a single gas molecule adsorbed on the solid. For an hexagonal closed-packed nitrogen monolayer, **s** is 16.2 Å at 77.3 K [63]. The specific surface area (SSA) for the known mass of dry sample (M) can be calculated from the BET surface area, as follows.

$$SSA = \frac{S_{BET}}{M} \tag{8}$$

The (BET) equation could be written also as [63]:

$$\frac{1}{W(\left(\frac{P_0}{P}\right) - 1)} = \frac{1}{W_m C} + \frac{C+1}{W_m C} \left(\frac{P}{P_0}\right) \tag{9}$$

Where W is the weight of gas adsorbed at a relative pressure P/P_0 and W_m is the weight of adsorbate constituting a monolayer of surface coverage. The BET constant C is related to the adsorption energy of the first adsorbed layer and indicates the dimension of interaction between the adsorbate and adsorbent.

To determine the surface area using this equation, a linear plot of $1/(W(P_0/P)-1)$ vs. P/P_0 is required. This linear dependence is limited to a small P/P_0 range of usually 0.05 to 0.35, which shifts to lower values for microporous materials [64]

The first BET measurements were performed by Dr. Angelos Polyzoidis at the ICT. Nitrogen adsorption isotherms were measured at -196 °C using a Quantachrome Autosorb iQ surface area analyser. Samples were degassed under vacuum for 16 h at 100 °C (MOFs) or 180 °C (pyrolyzed samples) prior to the analysis. BET pressure range varied between $3.0 \cdot 10^{-2}$ and $7.0 \cdot 10^{-2}$ bar for the MOF samples and 0.1 and 0.3 for the pyrolyzed samples.

The second BET measurements and N₂ sorption measurements were performed by Lina Rustam from the Fraunhofer-Institut für Solare Energiesysteme ISE.

4 Experimental Setup and Procedure

4.1 Fibers

4.1.1 Electrospinning

Experimental Layout

For the production of the fibers, an electrospinner Model E-Fiber EF100 from the company SKE Research Equipment was used. Figure 14 shows the electrospinner setup with its main 3 components:

- the high voltage power supply
- a syringe pump
- the collector



Figure 14: Electrospinner setup. (a) Hole setup placed inside a Plastic box. (b) Pump and syringe. (c) Needle connected to the voltage supply and mat of fibers over plate collector.

This setup is placed inside a Plastic box with a fume and an inlet of dry air.

It could be seen in Figure 14b that a syringe filled with the polymer solution is mounted on the pump. From the pump the volume flow could be adjusted and it also shows the volume dispensed. Plastic syringes with 12 ml of volume were used.

To the syringe is connected a pipe and a needle. For the experiments with PVP, the pipe was a Tygon tube of 1 mm of inner diameter. For the ones with PAN, a PEEK tube was used as the pipe since swelling and leaking was observed during the experiment with the Tygon tube. The needle had 1 mm of diameter.

The high voltage supply is connected to the needle by an alligator clip connector.

The collector used in most of the cases was a plate collector of 12 x 13 cm and it was covered with an aluminum foil.

As it could be also seen in the figure, the electrospinner box has a control panel where it could be chosen the set point for Voltage, Humidity and Rotation speed (in case of rotating collector). Also, it could be seen the instant humidity and temperature inside the box.

To control the humidity, a dehumidifier Trotec TTR 400 D was connected.

Experimental Procedure

As mentioned before, the polymer fibers are electrospun from a precursor solution. For this purpose, different precursor solutions were prepared.

The following materials were used to prepare the solutions (Table 4).

Material	Company	Molecular weight
Polyvinylpyrrolidone		
(PVP)	Alfa Aesar	1.300.000
Polyacrylonitrile (PAN)	Aldrich	150.000
Methanol (MeOH)	Roth	-
Ethanol (EtOH) Absolute	CHEMSOLUTE	-
N,N-Dimethylformamide		
(DMF)	Merk	-

Ni-MOF-74 + PVP + MeOH solution (for the Combined catalyst synthesis)

1.5 g PVP was dissolved in 20 mL of MeOH. Additionally, 309 mg of Ni-MOF74 was homogenized in 17.5 mL of MeOH. Afterwards, both solutions were combined. The solution obtained had a relation of MOF/PVP of 1/5 and the concentration of the solids (MOF+PVP) in the solution was 5.7 wt %.

PVP + MeOH solutions

PVP powder was dissolved in MeOH at various weight percentages (4 wt %, 6 wt % and 8 wt %) under ultrasonic bath for 15 min and then under magnetic stirring for 4 h at 700 rpm and room temperature. In all the cases the solution was stirred for extra 15-30 min before the electrospinning.

PVP + EtOH solutions

PVP powder was dissolved in EtOH at various weight percentages (4 wt %, 6 wt % and 8 wt %) under magnetic stirring for 15 h at 600 rpm and room temperature. In all the cases the solution was stirred for extra 15-30 min before the electrospinning.

PVP + EtOH/DMF solutions

PVP powder was dissolved in a mixture of EtOH and DMF with a mass ratio of 50/50 under magnetic stirring for 15 h at 600 rpm and room temperature. In all the cases the solution was stirred for extra 15-30 min before the electrospinning.

PAN and DMF solutions

PAN powder was dissolved in DMF under magnetic stirring for 4 h at 400 rpm and 60 °C. The solution was stirred for extra 15 min at room temperature before the electrospinning.

Also, a detailed protocol for the electrospinner operation is included in the Appendix.

Experimental Matrix

As a first approach, a "Combined catalyst synthesis" was investigated. Thus, it was tested to include the MOFs in the polymer precursor solution prior to electrospinning, under the technique of "direct electrospinning" [32]. For this purpose, a solution of Ni-MOF74, PVP and MeOH was prepared and electrospun.

The parameters for the electrospinning were the following:

- Feeding rate: 1.2 ml/h
- Applied Voltage: 15 kV
- Distance of collector from tip of the needle: 12.5 cm
- Type of collector: Plate
- Humidity: 32-38 %

After the pyrolyzation of the fibers, the result was not the expected (no carbon fibers were obtained). There were many parameters that could be responsible for the observed, from both sides, fibers and MOFs. In order to address this. each part was analyzed and optimized separately and then combined, as a "Three step catalyst synthesis".

To understand better the electrospinning process, some of the controlling parameters were varied. It was chosen the parameters that had the greatest impact on fiber morphology, as reported in the literature [39,42]. Those parameters were the polymer concentration and the solvent in the precursor solution and the applied voltage during the electrospinning. Then, the polymer of the precursor solution was also varied.

Other parameters were kept constant with the following values:

- Feeding rate: 1.2 ml/h
- Distance of collector from tip of the needle: 12.5 cm
- Type of collector: Plate
- Humidity: 32-38 %

As a reference, some parameters were taken from previous experiments conducted at ICT with the electrospinner, like the feeding rate of the polymer solution and the distance from the tip of the needle to the collector, since they proved to be suitable for a similar polymer solvent systems. Since an array of aligned fibers is not necessary in this case of study, the plate collector was chosen for the experiments.

PVP as the polymer, MeOH as the solvent and 15 kV as the applied voltage (plus same distance tipcollector) were also taken as a reference from previous experience at the ICT, since they showed to be good parameters for the electrospinning of fibers and posterior calcination.

Concentration variation

It was varied the concentration of a PVP-MeOH solution and also of a PVP-EtOH solution between the following values:

Concentration 1	Concentration 2	Concentration 3
4 wt %	6 wt %	8 wt %

It was found difficulties during the electrospinning for a solution of PVP and MeOH with higher concentration than 8 wt %, so there were chosen concentrations below that value.

This concentrations were used in the literature for the electrospinning of a solution of PVP and EtOH [42] and also a concentration in the range was used to prepare a precursor solution of PVP and MeOH to produce PVP fibers for electrochemical application [49], both cases with similar parameters for electrospinning.

Solvent variation

Solvent 1	Solvent 2	Solvent 3
Methanol	Ethanol	Ethanol/DMF 50/50 (w/w)

MeOH was used at ICT with PVP for the electrospinning and worked as a good solvent. EtOH was mentioned in the literature to be a good solvent for PVP [42] and it is preferred over MeOH to be easier for handling. The mixture of solvents EtOH/DMF with a mass ratio 50/50 showed to be a good dissolvent for PVP, producing thinner fibers and a uniform size distribution [42].

Voltage variation

Voltage 1	Voltage 2	Voltage 3
11 kV	13 kV	15 kV

15 kV was the voltage used in the previous experiment, so it was chosen as a fixed parameter for the concentration and solvent variation electrospinning. Since in other publications 15 kV or lower voltages were applied, there were chosen smaller voltage values to be tested, in those ranges [42,49].

Polymer variation

Apart from the PVP, PAN was used for the preparation of the precursor solution.

The concentration of the precursor solution was 8 wt % and the applied voltage for the electrospinning was 15 kV. This, were common values among the literature for PAN fibers [36] and were chosen because of the experimental experience with PVP, that will be discussed later.

4.1.2 Heating Process

Experimental Layout

The electrospun polymer fibers were exposed to a heating process in order to obtain carbon fibers. For this purpose, a tube furnace Carbolite type HST 12/400 with an Eurotherm 3216 controller was used (Figure 15).



Figure 15: Tube furnance

The oven could reach 1200 °C as maximum temperature. A quartz tube is mounted inside the furnace, which is open at one end to place the crucible with the sample. The tube has a lid and it is possible to connect a gas inlet and a gas outlet at both ends. This allows to seal the tube with a controlled atmosphere.

Experimental protocol

Several programs combined with different gas atmospheres were used.

For the "Combined catalyst synthesis" (fibers of PVP and Ni-MOF74), the following combination of program of heating and gas atmosphere was used:

- Program 1 of heating, showed in Figure 16, and synthetic air
- Program 2 of heating, showed in Figure 17, and Ar
- Program 2 of heating and N₂



The Program 2 of pyrolysis was designed following the literature [49].

For the PVP fibers, the program 3 of heating (Figure 18) and N2 atmosphere was used. For this program it was considered the result of the TGA of the PVP fibers, that is showed in the chapter of Results and Discussion.



Figure 18: Program 3 of heating

At the beginning, the tube was flushed with N_2 for 30 min to remove the air inside the tube before increasing the temperature. The flushing will also continue during the next step, which is maintaining the temperature in 60 °C for 4 h to make the moisture and the MeOH absorbed by the PVP to go out. The first step is followed by a slow heating ramp, to let the remaining moisture leave the sample without affecting the structure. Then the temperature is maintained at 400 °C for 1 h and this is

continued with slow heating ramp until 500 °C, since the TGA showed that there is a big mass loss between 375 °C and 475 °C. The mass loss from 500 °C onwards is significantly lower, so a higher heating rate is applied, until 1000 °C. The final temperature of the program was raised to 1000 °C.

The program 4 was also used for the PVP fibers. It is like Program 3, but the first step is replaced by a longer one: the temperature is kept at 80 °C for 24 h. The program 4 run with N_2 atmosphere too.



For the PAN fibers the program 5 of heating (Figure 19) and nitrogen atmosphere was used.



In this case, the step for drying was kept for 4 h, since the PAN did not have a big amount of moisture absorbed. After that, a program from the literature for PAN fibers was followed [53]. The temperature was raised at a heating rate of 120 °C h⁻¹ until 350 °C where it was stabilized for 20 min. Then, the temperature was further raised at a heating rate of 300 °C/h to 1000 °C, to have a good conductivity, and the film was carbonized for 2 h to obtain carbon fibers.

4.2 Metal Organic Frameworks (MOFs)

For this work five MOF-74s with different nickel-cobalt content were successfully synthesized by the group of Dr. Piscopo of the Energetic Materials group at ICT. All the details about the synthesis were provided by them.

The MOFs prepared are based on 2,5-dihydroxyterephthalic acid (DOT) and nickel and cobalt in different ratios [28]. The details of the synthesis of each MOF-74 could be found in the Appendix.

The MOFs prepared were the following:

- Ni-MOF74 (pure nickel-MOF74)
- Ni₇₅Co₂₅-MOF74 (ratio Ni:Co 3:1)
- Ni₅₀Co₅₀-MOF74 (ratio Ni:Co 1:1)
- Ni₂₅Co₇₅-MOF74 (ratio Ni:Co 1:3)
- Co-MOF74 (pure cobalt-MOF74)

The MOFs were characterized by XRD, BET, TGA, and SEM before and after pyrolysis to compare its change and the differences between the different MOFs.

Heating process

The MOFs were pyrolyzed under nitrogen atmosphere and the same tube furnace used for the fibers, with the following heating program:

- 1) 1 h of flushing the tube with nitrogen
- 2) heating rate of 100 °C/h until 700 °C
- 3) 6 h at 700 °C

The maximum temperature of pyrolyzation of the MOFs (700 °C) was decided as a compromise between not destroying completely the structure of the MOFs [26,65] and obtaining the higher carbonization possible [65].

4.3 Catalyst Production

For the production of the supported catalyst the following protocol was followed:

- 1. A portion of the fibers pyrolyzed until 1000 °C (80.30 mg) was mixed with the chosen MOF (Ni-MOF74) without pyrolyzation (210,4 mg) and (10,52 ml).
- 2. The quantities correspond to a relation mass of 3/4 of MOFs over PAN fibers without pyrolyzation (280,97 mg), which means a relation of 2,62 times of MOFs over the pyrolyzed fibers. The volume of Ethanol was calculated as 1 ml of Ethanol per 20 mg of MOF and per 25 mg of total mass.
- 3. The three components were added into a 40 ml bottle and homogenized in a Sonifier Branson 250 with an ultrasonic horn of 3 mm of diameter under the following program:
 - Energy per pulse: 12 J
 - Time between pulse: 00⁵⁰ sec
 - o Total energy: 2500 J
 - T measurement: 50 °C
 - o Amplitude: 25 %
- 4. During the sonication, the tube was submerged into ice and liquid water, to avoid the mixture to heat up.
- 5. The sonication was repeated 3 times, refilling the ice in between the repetitions. The "T measurement: 50 °C" was set to make the sonication stop in case the Temperature reaches 50 °C, but it was never the case. Heating the suspension over 60 °C should be avoided, since the liquid absorbed by the MOF could destroy the MOF structure while gaining energy.
- 6. The suspension was filtered with vacuum (up to 300-400 mbar). The set up used for this step is showed in Figure 20a, which consisted of a Büchner funnel with a filter inside, over a Büchner flask connected to vacuum. The filter mentioned is a Polyethersulfone (PES) membrane with a pore size of 0.45 μm.
- 7. In less than 5 minutes the filtration was finished. The ethanol collected in the Büchner flask looked transparent, indicating that most of the supported catalyst was retained by the filter.
- 8. The filter cake was collected from the paper filter and placed in a 25 ml round bottom single neck Schlenk flask with a glass stopcock (Figure 20b), connected to the vacuum line. Vacuum at 260 mbar was applied at room temperature for 4 h 40 min.





Figure 20: a) Set up for the filtration with vacuum; b) Set up for the extraction of liquid with vacuum.

- 9. The round bottom Schlenk flask was placed inside an oil bath to heat up the powder while continuing with the application of vacuum. The heat was applied to help the remaining liquid to leave. It was applied gradually, in steps of 10 °C for less than 10 min, from 40 °C until 80 °C. To finish the liquid extraction by vacuum, it was kept for 30 min at 80 °C.
- 10. The stopcock of the Schlenk flask was closed and the lid opened, to take out the dry catalyst.
- 11. The dry catalyst was pyrolyzed under Nitrogen atmosphere, with the same program used to pyrolyze the MOFs.

Scaling up

To produce a batch of the supported catalyst (PAN-Ni-MOF74) for the test in a cell, a higher loading of MOFs over the fibers was applied. In this case, a relation of 4/4 of MOFs over PAN fibers without pyrolyzation was considered (which means an amount of 3,38 times of MOFs over the pyrolyzed fibers). 1470,09 mg of MOFs were mixed with 435,45 mg of pyrolyzed PAN fibers (until 1000 °C) and 68,96 ml of Ethanol, giving a scaling up of 6,6 times of total mass from the first batch. A relation of 1ml per 25 mg of total mass was considered for the Ethanol since the ratio MOF/fibers is different.

To mix the components, the same program of sonication was performed. In this case the program was repeated 19 times, to maintain the relation of total anergy applied over total mass.

The suspension was filtered and connected to vacuum, with the same materials and times as the first batch.

The vacuum applied at room temperature reached the 160 mbar in this case, for 4 h 40 min and for the step of vacuum and heating, it was between 220 and 235 mbar.

As an improvement, after the extraction of the liquid, the Schlenk flask was filled with N_2 , for weighting and transportation to the oven, to avoid moisture to be absorbed in that time. This effect wasn't considered in the smaller batch produced.

The dry catalyst was pyrolyzed with the same program mentioned before.

5 Results and discussion

5.1 Physicochemical characterization

5.1.1 Fibers

5.1.1.1 Combined catalyst synthesis

As a first approach, a "Combined catalyst synthesis" was investigated. It was reported from the literature [49] a combination of PVP, methanol and a different MOF by this technique with good results for an energy application.

As mentioned in the previous section, a solution of Ni-MOF74, PVP and Methanol was prepared and electrospun. In Figure 21 SEM images of the electrospun fibers are showed.



Figure 21: SEM images of electrospun fibers from a Ni-MOF74, PVP and Methanol solution.

It could be observed that the fibers had white agglomerations that could be attributed to the MOFs or a beaded formation.

5.1.1.2 SEM - Variation of electrospinning parameters

A series of electrospinnings were carried out, varying the parameters mentioned in Section 4. The mat obtained were analyzed by SEM. In the following Section those results will be discussed.

Concentration variation

From solutions of Methanol and different concentrations of PVP, fibers were electrospun. In Figure 22

SEM images of the mat obtained are showed.





(c) Figure 22: SEM images of electrospun fibers from a solution PVP-Methanol (a) 4 wt %, (b) 6 wt % and (c) 8 wt % (10 K x of magnification).

Form Figure 22 it could be seen that there is a formation of beads that decreases with the increase of concentration. For the case of 4 wt % PVP-Methanol solution, there are a lot of sphere-like beads on the fibers, while for the case of 6 wt % the beads are less and look elongated. The fibers from the 8 wt % solution are mostly smooth with eventually some elongated spindle-like beads.

Some diameters of the fibers were measured to obtain an estimation of the size of the fibers. In Table 5 it could be seen that the range of diameters is not very wide. The diameter of the fibers increases with increasing concentration of the precursor solution, as it was mentioned by other authors [42,51].

	MeOH+PVP 4 wt %	MeOH+PVP 6 wt %	MeOH+PVP 8 wt %	
MIN (nm)	72.3	96.8	162.1	
MAX (nm)	255.5	270.5	319.7	
AVERAGE (nm)	139.9	181.6	243.6	

Table 5: Diameters of the fibers from PVP-Methanol solutions of 4 wt %, 6 wt % and 8 wt % of concentration

It was also varied the concentration of PVP in another solvent: Ethanol. The chosen concentrations were also 4 wt %, 6 wt % and 8 wt %. In Figure 23 are showed SEM images of the mat obtained.





Figure 23: SEM images of electrospun fibers from a PVP-Ethanol solution (a) 4 wt %, (b) 6 wt % and (c) 8 wt % (10 K x of magnification)

It could be seen that the behavior regarding the beads and the diameters is similar to the Methanol-PVP solution. There is a decrease in the amount of beads formed when the concentration of the precursor solution is increased, and the shape of them also tends to elongate.

For the case of 4 wt % the fibers have a big number of beads on them, with a sphere-like shape mostly. For the case of fibers from 6 wt % solution, there is a smaller amount of beads on the fibers, but this beads have a bigger size. For the fibers coming from the 8 wt % solution, it could not be observed bead formation, but some small differences in the diameter of the fiber. Table 6 shows a summary of the measured fiber diameters for the ethanol PVP solutions.

	EtOH+PVP 4 wt %	EtOH+PVP 6 wt %	EtOH+PVP 8 wt %
MIN (nm)	83.9	211.2	678.0
MAX (nm)	231.6	724.5	1,736.8
AVERAGE (nm)	146.3	433.3	1280.2

|--|

It can be seen that there is an increase in the average diameter of the fiber with the increasing concentration of the precursor solution. But in this case, compared to the fibers from the MeOH-PVP solutions, the increase in the average diameter of the fibers with increasing concentration is much greater.

Also, the diameter deviation increases with increasing concentrations, ending with a very wide range for the case of 8 wt %.

Solvent variation

Since it was observed that with solutions of 8 wt %, the fibers obtained had less or none beads, it was the chosen concentration to be fixed for the solvent variation.

As it was mentioned in Chapter 4, the third solvent, apart from Methanol and Ethanol, was a mixed solvent: Ethanol/DMF, with a mass ratio of 50/50. This mixed solvent was mentioned by Yang [42] to be a very good option since it combines desirably properties from each solvent, to produce thin fibers with no beaded formation.



(b)



Figure 24: SEM images of electrospun fibers from a solution of PVP and (a) Methanol, (b) Ethanol, (c) Ethanol/DMF 50/50 w/w, with 8 wt % of concentration (10 K x of magnification).

Regarding the diameters of the fibers, it could be seen (Table 7) that the fibers obtained from the Ethanol solution have a much greater diameter compared to the Methanol ones. As was expected [42], the addition of DMF to the Ethanol, made the fibers obtained to have a lower diameter without the generation of beads.

Table 7: Diameters of the fibers from a solution of PVP and Methanol, PVP and Ethanol and PVP and Ethanol/DMF 50/50w/w, with 8 wt % of concentration

	MeOH+PVP 8 wt %	EtOH+PVP 8 wt %	DMF/EtOH+PVP 8 wt %
MIN (nm)	162.1	678.0	167.5
MAX (nm)	319.7	1,736.8	412.4
AVERAGE (nm)	243.6	1280.2	315.1

Voltage variation

For the voltage variation, the mixed solvent Ethanol/DMF (50/50 w/w) was chosen to prepare the precursor solution with PVP. As seen in the previous section, the fibers obtained from this solution showed to be smooth and to have a small diameter in combination with a very low amount or almost no beads on the fibers.

In Figure 25 are showed SEM images of the fibers obtained at 10 K x.



Figure 25: SEM images of electrospun fibers from a solution of PVP and Ethanol/DMF 50/50 w/w, with 8 wt % of concentration at (a)11 kV, (b) 13 kV, and (c) 15 kV (10 K x of magnification).

It could be seen that there is no tendency of behavior of the mean diameters. This may be explained by the viscosity not being high enough for the voltage to significantly affect the fibers. Gomes et al. [36] showed, while studying the effect of the applied voltage in the fiber diameter, that the diameter variation is less pronounced for the fibers obtained from less viscous solutions independently of the applied voltage.

11 KV, 13KV dha 15 KV oj voltage.				
	DMF/EtOH+PVP 11kV	DMF/EtOH+PVP 13 kV	DMF/EtOH+PVP 15 kV	
MIN (nm)	106.5	133.5	167.5	
MAX (nm)	471.2	470.4	412.4	
AVERAGE (nm)	278.2	265.4	315.1	

Table 8: Diameters of the fibers from a solution of PVP and Ethanol/DMF 50/50 w/w, with 8 wt % of concentration for 11 kV. 13kV and 15 kV of voltage.



Figure 26: SEM images of electrospun fibers from a solution of PVP and Ethanol/DMF 50/50 w/w, with 8 wt % of concentration at (a)11 kV, (b) 13 kV, and (c) 15 kV (2 K x of magnification).

From the SEM images with lower magnification (Figure 26) it could be seen that there are some beads on the fibers. For the case of lower voltages (11 kV and 13 kV) there is a higher concentration of beads compared to the 15 kV images. Gomes et al. also reported that fibers with beads and irregular shape were obtained under low applied voltages [36].

Polymer variation

Since the results of the pyrolyzation of the PVP fibers were not successful (see next Section), PAN fibers were produced. To prepare the precursor solution, the solvent DMF was used. The other solvents considered in the previous Section (Ethanol, Methanol) could not be used because they are not solvents for PAN [66]. DMF is one of the aprotic polar solvents that can dissolve PAN and also forms a good solution to be electrospun [67].

As a concentration of the precursor solution of 8 wt % and an applied voltage of 15 kV were found to be good parameters for the electrospinning of the PVP fibers, these parameters were chosen for the electrospinning of a PAN solution.



Figure 27: SEM images of electrospun fibers from a solution of PAN and DMF with 8 wt % of concentration with (a)10 K x, (b) 5 K x and (c) 40 K x of magnification.

In Figure 27 some SEM images of the PAN-fibers obtained at different magnifications are showed. It could be seen that the fibers are uniform in its diameter and they present a very small amount of beads on them compared to the PVP fibers.

In Table 9 are showed the results of the diameter estimation for the PAN fibers, compared with the results already showed of the PVP fibers. The PAN fibers have the smallest average diameter even though it is in the order of the one of Methanol-PVP fibers and of DMF/EtOH-PVP as well. Also, the deviation of diameters of the PAN fibers is not wide, giving the idea that the sizes of fiber are more homogenous, compared to the PVP fibers. Figure 48 of the Appendix illustrates qualitatively that the PAN fibers are the thinnest.

Table 9: Diameters of the fibers from a solution of PAN and DMF, compared with the ones of a solution of PVP and Methanol,
PVP and Ethanol and PVP and Ethanol/DMF 50/50 w/w (all of them with 8 wt % of concentration).

	DMF+PAN 8 wt %	MeOH+PVP 8 wt % EtOH+PVP 8 wt %		DMF/EtOH+PVP 8 wt %
MIN (nm)	168.8	162.1	678.0	167.5
MAX (nm)	224.8	319.7	1,736.8	412.4
AVERAGE (nm)	187.2	243.6	1280.2	315.1

Therefore, PAN fibers, besides being more suitable for the pyrolyzation stage, have a smaller diameter, which is desirable since it increases the surface area.

5.1.1.3 TGA and SEM after heating process

PVP fibers



In the following the results of the Thermogravimetric Analysis (TGA) are showed.

Figure 28: TGA of PVP fibers under N₂ atmosphere

A 3-fold determination was carried out, as the sample fluctuates in the lower temperature range up to 120 °C. The result of the two additional measurements could be found in the Appendix. The sample was analyzed in the autosampler. It is possible that traces of methanol were still present, which evaporates during the standing time on the autosampler.

The measurement showed in Figure 28 was started immediately after weighing.

The TG curve shows a mass loss of 17.10 % between 25 °C and 120 °C that represents the loss of residual methanol. The point of greatest rate of change on the initial part of the weight loss curve ocurrs between 60 °C and 75 °C, which corresponds with the boiling point of the methanol at 64.7 °C [68]. At that point a mass loss around 10 % could be observed.

Also, it could be seen a sharp decline between 375 °C and 475 °C, indicating a notable weight loss of 73.8 % due to the thermal decomposition of PVP [69].

Between 500 °C and 1000 °C there is negligible mass loss. After 1000 °C the remaining mass is 5 %.

Several pyrolyzations of the PVP fibers under different atmospheres were carried out looking forward to obtain pyrolyzed fibers. Also, different programs of pyrolysis were used.

Some SEM images of PVP+Ni-MOF74 fibers ("Combined catalyst synthesis") after the pyrolyzation/calcination are showed in Figure 29.



Figure 29: SEM images after pyrolyzation of PVP+Ni-MOF74 fibers under (a) Air (Program 1), (b) Argon (Program 2) and (c) Nitrogen (Program 2) atmosphere, from a solution of PVP, Methanol and Ni-MOF74.

As it could be observed, no fibers were found after pyrolysis.

It was previously reported in the literature by Lai et al. that a methanolic solution of PVP and ZIF-8 (a type of MOF) was electrospun and heated up to 900 °C in N_2 atmosphere, successfully obtaining fibers after both processes. It was the interfacial interaction between PVP and ZIF-8 that changed the pyrolysis behaviors and promotes the formation porous structures.

They proposed a mechanism where the Zn²⁺ sites of the surface of the ZIF-8 were coordinated easily with C=O existing in PVP, and after being calcinated at 500 °C, the PVP in the mixture decomposed to an amorphous carbon network, while the ZIF-8 polyhedrons retained their crystal structure. Due to the low pyrolysis temperature, the PVP-derived carbon still had many C=O bonds that could form a new but strong interface with the ZIF-8 [49].

In our case it could be assumed that no coordination bonds could be formed between the PVP and the Ni-MOF74 to maintain a crystal structure. It may have been the case that the sites of Ni²⁺ were not accessible to the PVP.

The program of pyrolyzation was changed following the information from TGA (Program 3).

The final temperature of the program was raised to 1000 °C since it was reported that higher temperatures of pyrolysis for carbon substrates lead to higher conductivity [65], which is a desirable property for the fibers.

The result is showed in Figure 30.



Figure 30: SEM image after pyrolyzation of PVP fibers from a solution PVP+Ethanol 8 wt % (Program 3 of heating).

The PVP fibers were also pyrolyzed under the program 4 with N₂ atmosphere. In this case the first step was replaced by a longer one: the temperature is kept at 80 °C for 24 h [70]. Since the PVP is more polar it attracts the water molecules strongly, so the 4 h of drying in Program 3 might not be enough to complete the drying step. It could be observed, comparing the TGA of PVP fibers and PAN fibers that is showed in the following, that the PVP has a higher mass loss before 100 °C, which shows this higher water absorption by PVP.

However, no fibers were obtained after pyrolyzation (Figure 31).



Figure 31: SEM images after pyrolyzation of PVP fibers from a solution (a) PVP+Ethanol 8 wt % and (b) PVP+Methanol 8 wt % (Program 4 of heating).

These results could be explained by the thermal degradation of the PVP under N_2 atmosphere, where the predominant mechanism is the depolymerization to monomer of the polymeric main chain [71] (Figure 32).



Figure 32: Suggested mechanism for thermal degradation of PVP [71]



PAN fibers

A TGA was performed to the PAN fibers.

Figure 33: Thermogram of PAN fibers under N₂

The sample showed an initial mass loss of approx. 1.4 % in the temperature range of 60 - 140 °C, that is related with the remaining moisture. The main decomposition of the sample proceeds in two stages. In the temperature range 200 - 330 °C the mass loss is 48 / 48.3 %, up to 500 °C further 15.9 / 16.3 %.

The mass loss in the first step may be attributed to the cyclization reaction because micromolecular gases such as HCN, H2O, and H2 could have escaped from PAN due to the cyclization. During further heating to the final temperature of 1000 °C, the sample loses a further 11.4 / 12.9 % of mass. The residual mass is finally 21.5 / 22.9 %.

The program for pyrolyzation of the PAN fibers was obtained from the literature before the result of the TGA was ready. This result could be considered for future experiments, for example in lowering the stabilization temperature to 250 °C-280 °C.

The PAN fibers obtained were exposed to the heating process mentioned in the previous Section. In Figure 34 are showed SEM images of the result. It could be seen that fibers were obtained after the pyrolyzation and remain with a similar shape. Figure 35 is a crop of one of the SEM images of the pyrolyzed fibers, and it shows that section of the fiber is circular.



Figure 34: SEM images of pyrolyzed PAN fibers with (a)10 K x, (b) 5 K x and (c) 40 K x of magnification.



Figure 35: SEM image of section of pyrolyzed PAN fiber

In Figure 49 of Appendix SEM images before and after pyrolyzation are showed, for comparison.

Table 10 shows the diameter estimation for the pyrolyzed fibers compared with the values for the fibers before pyrolyzation. It could be seen that there is a shrinkage of the fibers during the pyrolysis, which means a reduction of the 50 % of the cross-section area of the fibers.

	DMF+PAN 8 wt % pyro	DMF+PAN 8 wt %
MIN (nm)	114.9	168.8
MAX (nm)	155.4	224.8
AVERAGE (nm)	132.7	187.2

Table 10: Diameters of pyrolyzed PAN fibers, compared with the diametrs of the PAN fiber before pyrolyzation.

It would be interesting to try, in future experiments, to make the stabilization step under air atmosphere (and adapt the program), since it was found that fibers stabilized with air showed better carbon yield [72], a property desired for the conductivity of the fibers.

5.1.2 MOFs

In the following section results from the analysis performed to the MOFs will be presented.

The MOFs were pyrolyzed with the program mentioned in the previous Section under N₂ atmosphere. The proportions of mass of MOF74 that was lost after pyrolysis are the following: 66 % for the Ni-MOF74, 67 % for the Ni₇₅Co₂₅-MOF74, 68 % for the Ni₅₀Co₅₀-MOF74, 68 % for the Ni₂₅Co₇₅-MOF74 and 70 % for the Co-MOF74.

In Figure 36 the TGA of Ni-MOF74 is showed and in Figure 51 of Appendix could be found the TGA of the other 4 MOFs synthetized.



The first weight loss step is attributed to the removal of occluded and coordinated water molecules. Therefore, the MOF can be called stable up to 250 °C. The second weight loss (approximately 300 °C) is related to the decomposition of organic linkers and the residual weight percent is assigned to the remaining metal oxides [30].

The mass loss observed after the pyrolyzation of the MOFs is similar to the ones observed in the TGA until 700 °C.

Regarding the temperature of pryrolyzation, it could happen that the Ni acted as a catalyst for the carbonization, and the pyrolysis could be done until a lower temperature. This could be tested and optimized in future projects.

The crystallinity of the framework compounds was confirmed by XRD measurements. The XRD diffractogram of Ni-MOF-74 before and after pyrolysis is showed in *Figure 37*. It could be seen that after pyrolysis there is no crystalline framework anymore.



Figure 37: XRD diffractogram of Ni-MOF-74 (a) before pyrolysis and (b) after pyrolysis.

The BET surface areas of the MOFs (before pyrolysis) are summarized in Table 11. All the prepared materials have surface areas consistent with those reported in the literature.

MOF	BET - MOF Before pyrolyzation	BET - MOF After pyrolyzation (m ² /g)
	(m²/g)	
Ni-MOF74	464	-
Ni ₇₅ Co ₂₅ -MOF74	661	200
Ni ₅₀ Co ₅₀ -MOF74	686	228
Ni ₂₅ Co ₇₅ -MOF74	462	-
Co-MOF74	274	-

It was also measured in the same conditions, the BET surface area of two of the MOFs after pyrolyzation. It could be observed that there was a surface reduction of the 67 % for the Ni₅₀Co₅₀-MOF74 and of 70 % for the Ni₇₅Co₂₅-MOF74.

The porosities of the MOFs after pyrolysis were investigated doing N₂ sorption measurements. The results of the corresponding BET surface areas are showed in Table 12.

TUDIE 12. BLT SUTJUCE UTEUS OJ TITE PYTOTYZEU MOFS					
MOFs pyrolyzed	BET (m²/g)				
Ni-MOF74	189.220				
Ni ₇₅ Co ₂₅ -MOF74	186.447				
Ni ₅₀ Co ₅₀ -MOF74	195.094				
Ni ₂₅ Co ₇₅ -MOF74	235.123				
Co-MOF74	275.356				

Table 12: BET	surface	areas	of the	pyrolyzed	MOFs

Ni₂₅Co₇₅-MOF74 and Co-MOF74 have a larger amount of micropores resulting in higher surface areas.

SEM images were also taken. Figure 38 shows the comparison of all the MOF before and after pyrolysis at 25 K of magnification. SEM images with other magnifications could be found in the Appendix.











Figure 38: SEM images of the MOFs at 25 K of magnification. Before pyrolyzation: left side; after pyrolyzation right side. a, b) Ni-MOF74; c, d) Ni₇₅Co₂₅-MOF74; e, f) Ni₅₀Co₅₀-MOF74; g, h) Ni₂₅Co₇₅-MOF74; I, j) Co-MOF74

It could be observed that the Ni-MOF74 formed larger crystallites and the sample looks denser.

The combined Co-Ni MOFs and the Co-MOF74 look less dense which is in accordance with the higher surface area indicated in BET.

In Figure 39 it could be seen more clearly the change in morphology after pyrolysis of the Ni-MOF74.



Figure 39: SEM images of Ni-MOF74 at 50 K x of Magnification. Before pyrolyzation: left side; after pyrolyzation right side.

The incorporation of the metals into the materials was determined by ICP-OES measurements. These measurements were performed after pyrolysis.

Table 13: Results of ICP-OES of the pyrolyzed MOFs.

Sample	Co concentration [g/kg]	Ni concentration [g/kg]
Ni-MOF74	-	756.75
Ni ₇₅ Co ₂₅ -MOF74	163.35	572.85
Ni50Co50-MOF74	369.15	369.7
Ni ₂₅ Co ₇₅ -MOF74	495.65	202.8
Co-MOF74	590.75	-

The results confirm that the metals were incorporated into the crystalline structure. However, it could be seen a tendency for the Cobalt to be in a small lower amount than expected. It might be because during the synthesis, the Cobalt was less absorbed by the material.

5.1.3 Fibers and MOFs combined

In the following, the results of the supported catalyst obtained after the procedure of combination of the fibers and the Ni-MOF74 (small batch), are showed.

After the combination and before the pyrolyzation a mass of 208 mg was obtained which was reduced into 99,38 mg after the pyrolyzation. Therefore, the mass loss was 52 %, that could be attributed mostly as a mass loss of the MOF.

In the case of the scaled-up batch, before the pyrolyzation a mass of 1547 mg was obtained. After pyrolyzation this mass was reduced into 805,7 mg with a mass loss of 48 %. This smaller mass loss could be explained partly because no moisture was absorbed during the weighting and transportation to the oven.

The results showed in the following correspond to the small batch. SEM images were obtained to observe which was the physical aspect of the supported catalyst. Also, EDS analysis was performed to detect if the Ni-MOF74 was homogeneously distributed, since this technique is capable of producing elemental distribution maps, like Nickel distribution map.

The SEM images (Figure 40) show that the fibers maintain its structure after the combination procedure and posterior pyrolyzation. It could be seen also that there are white agglomerations, smaller and bigger ones, over the fibers.





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Figure 40: SEM images of PAN fibers combined with Ni-MOF74 and pyrolyzed at 700 °C in N₂ atmosphere. (a)50 K x, (b) 10 K x and (c) 1 K x of magnification.

From the Nickel distribution map compared with the SEM image (Figure 41) it could be then assumed that those agglomerations correspond to the pyrolyzed Ni-MOF74 (Figure 53 and Figure 55 Appendix). Regarding the distribution of the pyrolyzed MOF, it could be seen (Figure 41a and Figure 52 Appendix) that besides to the agglomerations, there is presence of Nickel (pink dots) all along the fibers, however, the concentration is not homogeneous.

A way to improve this of the concentration could be to grind gently the MOFs and the fibers before the combination procedure, to help to disperse the possible MOFs agglomerations and to make more accessible for the MOFs to reach all the fibers. In the present procedure the mat of pyrolyzed fibers were broken with a glass stick in smaller parts, to help with the dispersion after 2 sonications, and after that an extra sonication was performed. The previous grinding of the MOFs wasn't considered since it could compromise the structure. Before pyrolyzation, the MOFs have coordination interactions [26], which are not very strong, and the MOF could be broken under high pressures. Nevertheless, a very soft grinding could be tried and then evaluate its impact.

It could be noticed also that the sample is mainly Carbon (Figure 41 and Figure 53 and Figure 55 from Appendix), coming from the pyrolyzed fibers and also from the structure of the pyrolyzed MOFs. From the ratio of elements obtained in different spots in the sample region showed in Figure 41b it could be noticed that in the dense bright pink areas the concentration of Nickel is high, corresponding to the white agglomerations already mentioned. Other points that have mixed colors in the overlapped

maps, are mainly carbon and a 10-30 % of Nickel and other points only carbon. The small amounts of Oxygen and Nitrogen could probably come from the MOFs that were pyrolyzed at lower temperatures under Nitrogen atmosphere. It could be seen that there were other elements detected in the sample (see Figure 41), but its concentration in all the points is very low and its overall presence is negligible.

PANgc04 01_a - AB3 - SE - 20kV - 50000x



PANgc04 01_a - AB2 - SE - 20kV - 5000x



EDS-Schichtbild - PANgc04 01_a - AB3 - 20kV - 50000x



(a)



Spectrum name	С	Ν	0	F	Na	К	Fe	Ni	Cu
Sp. 7 - PANgc04 01_a - AB2	> 80	5 - 10	1 - 4	< 1	< 1	< 0.1		< 5	< 1
Sp. 8 - PANgc04 01_a - AB2	> 90	5 - 10	1 - 4		< 1	< 0.1		< 1	
Sp. 9 - PANgc04 01_a - AB2	40 - 50		1 - 4					50 - 60	
Sp. 10 - PANgc04 01_a - AB2	60 - 70	< 5	1 - 4					20 - 30	
Sp. 11 - PANgc04 01_a - AB2	70 - 80	< 5	1 - 4		< 1			20 - 30	
Sp. 12 - PANgc04 01_a - AB2	70 - 80	5 - 10	1 - 4	< 1	< 1			10 - 20	
Sp. 13 - PANgc04 01_a - AB2	> 80	5 - 10	1 - 4		< 1	< 0.1		< 5	
Sp. 14 - PANgc04 01_a - AB2	70 - 80	< 5	1 - 4	< 1	< 1			10 - 20	< 1

(c)

Figure 41: EDS analysis of PAN+Ni-MOF74. (a) SEM and overlapped image of SEM and Ni distribution map of the same region. (b) SEM and overlapped image of C and Ni distribution map (of the same region) with spectra positions. (c) Ratio of elements found in 7 different positions, marked in b (data in w-%, ranges).
An ICP-OES was also performed to obtain the concentration of active material (Nickel) present in the combined catalyst. This result will be needed, combined with the electrochemical results, to calculate the mass activity.

Table 14: Results of ICP-OES of the combined fibers with Ni-MOF74 compared with pyrolyzed MOFs.		
Sample	Co concentration [g/kg]	Ni concentration [g/kg]
PAN+Ni-MOF74	0.04416	466.55
Ni-MOF74	-	756.75
Ni75Co25-MOF74	163.35	572.85
Ni ₅₀ Co ₅₀ -MOF74	369.15	369.7
Ni ₂₅ Co ₇₅ -MOF74	495.65	202.8
Co-MOF74	590.75	<bsg< td=""></bsg<>

The result is showed in Table 14, compared with the previous results from the pyrolyzed MOFs.

As expected, the concentration of active material in PAN+Ni-MOF74 is the lowest one and the concentration of Nickel is in between the one of $Ni_{75}Co_{25}$ -MOF74 and $Ni_{50}Co_{50}$ -MOF74.

5.2 Electrochemical characterization

5.2.1 Pyrolyzed MOFs

Cyclic voltammetry (CV) measurements were done to the pyrolyzed MOFs following the protocol mentioned in Section Analysis methodology.

The CV curves for cycles 1, 20 and 50 are showed in Figure 42 a, b and c. It could be seen that the mass activity of the different MOFs varies among the MOFs and the cycles.

In Figure 43 it is showed the mass activity at 1.6 V in different cycles for the five MOFs analyzed. This allows to observe the performance of the catalysts along the cycles.



Figure 42: CV curves of the 5 pyrolyzed MOFs for cycle (a) 1, (b) 20, and (c) 50.



Figure 43: Mass activity at 1.6 V in different cycles for the five MOFs analyzed.

It could be seen that in the first cycles, the MOFs with higher content of Cobalt have the highest activity, for example Co-MOF74 with 427 mA mg-1 followed by Ni₂₅Co₇₅-MOF74 with 281 mA mg-1. This could be also observed in the CV curves of the 1st cycle (Figure 42 a), where Co-MOF74 has the highest mass activity for all the potentials (V vs RHE) and the lowest onset potential.

However, from the 1^{st} cycle onwards the mass activity of both (Co-MOF74 and Ni₂₅Co₇₅-MOF74) decreases abruptly and after 14 cycles their activity falls down to 154 mA mg⁻¹, to be the lowest ones, compared to the other MOFs studied.

After that point both remain approximately constant. This is a behaviour commonly seen in other catalysts since there is usually a degradation in the catalyst after some cycles. Between cycle 26 and 35 there is a small increasing on the activity in both cases, to decrease linearly after that.

For the Ni₅₀Co₅₀-MOF74 case, it could be observed that the mass activity is relatively stable. Along all the cycles it is maintained between 245 mA mg⁻¹ and 278 mA mg⁻¹. This makes it the highest mass activity between the second and fifth cycle. From the cycle 6 onwards it becomes the second higher mass activity after Ni-MOF74.

On the other hand, the mass activity of the $Ni_{75}Co_{25}$ -MOF74 show to be lower than the other MOFs in cycle 1 with 140 mA mg-1 at 1.6 V vs RHE (Figure 43). It is also lower than the mass activity of the other MOFs along all the potentials in cycle 1 (Figure 42a). Additionally, the onset potential is higher than the other MOFs.

After the first cycle the mass activity increase (Figure 43), until cycle 5 with 242 mA mg⁻¹. From cycle 7 onwards it decreases gradually to be approximately constant between cycle 12 and 35 with a value between 200 mA mg⁻¹ and 2₂₅ mA mg⁻¹. After the 35th cycle the mass activity surpasses that range and increases linearly, reaching its higher value in the 50th cycle with 278 mA mg⁻¹.

The mass activity of the Ni-MOF74 along the first cycles, appear to be smaller than the other MOFs. Nevertheless after 6 cycles it becomes the one with higher activity with 279 mA mg⁻¹. From cycle 6 onwards the activity continues increasing along all the cycles, reaching 732 mA mg⁻¹ in the 50th cycle.

As it was mentioned for the mass activity at 1.6 V vs RHE, there is an increase and decrease of the mass activity for all the voltages and this change could be observed in Figure 42 from cycle 1 to cycle 20. In Figure 42 b and c (cycle 20 and 50) a similar behavior could be observed: the Ni-MOF74 exhibits the lowest onset potential, followed by Ni₇₅Co₂₅-MOF74 and Ni₅₀Co₅₀-MOF74 with a similar value. The highest on set potential is given by Ni₂₅Co₇₅-MOF74 and Co-MOF74 with a similar value as well

It would be interesting to do more cycles to evaluate if the activity of the Ni-MOF74 keeps increasing.

From these observations, it could be implied that the Cobalt suffers of a degradation along the cycles. In the other hand, with an opposite behavior, the Nickel has an activation as the cycles progressively increase.

The MOFs with pure content of one of the metals have clearly this performance and the ones with mixed content of Ni and Co, may be experiencing a competition between the effects of each metal. The Ni₅₀Co₅₀ could be showing a very stable activity because the degradation of the Co and the activation of the Ni are compensated.

The Ni₇₅Co₂₅-MOF74 does not adjust completely to this explanation. Activation possibly coming from nickel is observed during the first few cycles, but after that the curve would be expected to surpass the Ni₅₀Co₅₀ curve, and it does not occur. Since it's very close to it, it could be attributed to an experimental error, like temporary bubble forming under the electrode during the measurements. Therefore, the measurement should be repeated.

It is also interesting to observe in the CV curves, that there is a formation of peaks at low potentials. Figure 44 shows a zoom in this area of the graphs.





Figure 44: Zoom in at low potentials of the CV curves of (a) Ni-MOF74, (b) Ni₇₅Co₂₅-MOF74, (c) Ni₅₀Co₅₀-MOF74, and (d) Co-MOF74.

The formation of peaks seems to be related to the Ni. The peaks could be clearly seen in the Ni100-MOF graph (a), and after the proportion of Ni is decreased ($Ni_{75}Co_{25}$ -MOF74 and $Ni_{50}Co_{50}$ -MOF74) there is still some presence of the peaks, but they appear greatly reduced and smoothed. It could be thought that the Co inhibits the formation of these peaks.

It was observed by Thangavel et al. [13] that LSV curves showed a typical oxidation peak at 1.35 V (vs. reversible hydrogen electrode (RHE)) due to the transformation of Ni2+ to Ni3+ in alkaline solution, prior to OER. However, introducing Fe into Ni-BTC shifts the anodic peak (Ni2+/Ni3+) towards more positive values and its redox behavior is significantly affected.

It could be seen from Figure 44 that there are two peaks formed: one positive and another negative. The positive peak might be related to an oxidation occurring when the potential is increased and the negative peak, to a reduction when the potential is decreased back. [60] This may lead to the idea that there are other species formed while the experiment is conducted, and these species seem to have a very good activity.

It could be also observed that the area of both peaks increases as the cycles progress, leading to the idea that the amount of the redox species formed is bigger when the cycles are higher. This could occur because of a leaching of the carbon in the MOFs along the cycles, resulting in more active Ni sites being exposed.

This could be an explanation of the continuously increasing activity of the Ni-MOF74.

With the results exposed, the Ni-MOF74 was chosen to be combined with the fibers, since it showed the best activity along the cycles.

5.2.2 Nanofibers and MOFs combined

CV measurements were done to the combined Ni-MOF74 and PAN fibers. In Figure 45 could be seen the results obtained: a, b and c show the CV curves for cycles 1, 20 and 50 respectively, and Figure 46 shows the mass activity at 1.6 V in different cycles, compared with all the pyrolyzed MOFs.



Figure 45: CV curves of the PAN+Ni-MOF74 and the pyrolyzed Ni-MOF74 and Ni₅₀Co₅₀-MOF74 for cycle (a) 1, (b) 20, and (c) 50.



Figure 46: Mass activity at 1.6 V in different cycles for PAN+Ni-MOF74 and the five pyrolyzed MOFs.

In Figure 45 a, b and c the PAN+Ni-MOF74 curve was compared to the Ni-MOF74 and also to the $Ni_{50}Co_{50}$ -MOF74 for reference purposes. It could be seen that the PAN+Ni-MOF74 follows very well the behavior of the Ni-MOF74. This would suggest that during the process of combination, the catalyst is not affected. The activity of the combined catalyst is a bit smaller than the MOF alone, but it remains higher than all the other MOFs.

Focusing on the comparison between the combined PAN+Ni-MOF74 and the Ni-MOF74, Figure 46 shows that in all the cycles the activity of the supported catalyst is a bit lower than the MOF alone (142 mA mg⁻¹ vs 159 mA mg⁻¹ in cycle 2), becoming a bigger difference in higher cycles (466 mA mg⁻¹ vs 731 mA mg⁻¹ in cycle 50). And in graphs a, b and c (Figure 45) it could be seen that difference gets bigger for higher potentials than 1.6 V (vs RHE).

It could be also seen in Figure 46, that after cycle 30 the activity of the PAN+Ni-MOF74 appears to become constant at 1.6 V with a value between 480 mA mg⁻¹ and 500 mA mg⁻¹, while Ni-MOF74 continues increasing.

This could be also related with the formation of peaks already mentioned above. In Figure 47 a could be seen that the PAN+Ni-MOF74 shows the formation of peaks as the Ni-MOF74 alone showed. Along the cycles, it could be seen, that the area of the peaks in the PAN+Ni-MOF74 CV curve stop to increase after cycle 20/30. This leads to the idea that the peaks area becoming constant could be related with the approximately constant activity at 1.6 V.



(a) (b) Figure 47: Zoom in at low potentials of the CV curves of (a) PAN+Ni-MOF74, and (b) Ni-MOF74

6 Summary and Outlook

Water electrolysis is the simplest method to produce green hydrogen. The alkaline anion exchange membrane electrolysis (AEMWE) combines the advantages of the acidic polymer electrolyte membrane electrolysis (PEMWE) and the alkaline electrolysis (AEL) and at the same time eliminates their disadvantages [5,20]. However, the sluggish kinetics of the Oxygen evolution reaction (OER) at the anode is a bottleneck for water splitting efficiency [13].

For this purpose, supported catalysts for the oxygen evolution reaction (OER) were developed.

In this sense, a "Combined catalyst synthesis" was tested, electrospinning a methanolic solution of Polyvinylpyrrolidone (PVP) and a Ni-containing Metal Organic Framework (Ni-MOF74) with posterior pyrolyzation. It was showed that no fibers were obtained after the heating process.

Additionally, a "3 Step catalyst synthesis" was tested. In this case, the fiber production by electrospinning and the MOFs were analyzed and optimized separately and then combined.

As a first step, the effect of controlling parameters on the electrospun fiber size and morphology was studied. Therefore, polymer/PVP concentration, type of solvent and voltage were varied. It was found that an increasing concentration of the polymer solutions from 4 wt % to 8 wt % was correlated with an increase in the average diameter of the fibers. Beaded fibers were found in lower concentrations than 8 % wt. Regarding the type of solvent, thinner fibers were electrospun from a Methanol solution compared to Ethanol based solution. It could be observed that when the mixed solvent Ethanol/DMF 50/50 w/w was used, thinner fibers were obtained, with comparable diameter as the electrospun from Methanol. The average diameters of the fibers obtained after voltage variation showed no tendency, under the chosen conditions. The PVP fibers were pyrolyzed, showing no carbon fibers after this process.

Moreover, the variation of the polymer was also studied. Polyacrylonitrile (PAN) fibers were effectively electrospun from an 8 wt % solution with N,N-Dimethylformamide (DMF) under 15 kV with an average diameter of 187 nm. After pyrolyzation up to 1000 °C, carbon fibers were obtained. It was observed that the fibers suffered a shrinkage during the heating process, reducing its diameter to 132 nm approximately (-30% reduction).

Metal Organic Framework (MOF) with 5 different ratios of Nickel and Cobalt were characterized, physical, chemical, and electrochemically. These MOFs were pyrolyzed at 700 °C.

The OER performance of the MOFs was evaluated using Cyclic Voltammetry (CV) in a three-electrode setup. A rotating disk electrode (RDE) was used as working electrode in a 1 M aqueous KOH electrolyte with a scan rate of 10 mV s⁻¹ along 50 cycles.

Along the first cycle, the mass activity of the MOFs with higher content of Co was higher than the other MOFs. However, this behaviour was reversed as the cycles increased.

The MOF with higher content of Nickel (Ni-MOF74) showed higher mass activity than the other MOFs from cycle 6 onwards. The mass activity continued increasing along all the cycles, reaching

732 mA mg⁻¹ in the 50th cycle. The Ni₅₀Co₅₀-MOF74 showed to have a stable mass activity while the MOFs with higher content of Cobalt decrease in their mass activity to the lower one after 6 cycles.

Since the Ni-MOF74 showed the best activity along the cycles, it was chosen to be combined with the pyrolyzed PAN fibers.

Finally, a processing step was developed for the combination of the carbon fibers and the selected MOF by impregnation. Afterwards the supported catalyst (PAN+Ni-MOF74) was successfully produced and characterized.

It was observed that there was presence of Nickel along all the carbon fibers although some agglomerations of pyrolyzed MOFs were found. This could be improved in future experiments/investigations grinding the MOF gently before combination or increasing the energy applied during sonication. It could be also considered, including the MOF in the PAN solution for electrospinning to obtain composite fibers and posterior pyrolyzation. In this case it should be studied the effect of the temperature of pyrolyzation on the conductivity of the fibers and the structure of the MOFs.

The OER performance of the combined catalyst was studied with a Cyclic Voltammetry in the same setup and conditions as the pyrolyzed MOFs. The combined catalyst (PAN+Ni-MOF74) showed a similar behaviour as the pyrolyzed Ni-MOF74. The mass activity was lower than the other MOFs in the firsts cycles but from cycle 7 onwards it showed higher mass activity compared to the obtained with the MOFs with lower content of Nickel. The PAN+Ni-MOF74 had an increasing mass activity from the 1st cycle onwards experiencing activation, until cycle 30 when it stabilizes. Along all the cycles it had lower mass activity as the pyrolyzed Ni-MOF74. In future experiments increasing the content of MOF in the combined catalyst could be studied in order to obtain a higher mass activity, closer to the activity of the Ni-MOF74.

Summarizing, it was successfully studied two methods for the production of a supported catalyst based on Ni-MOF74 and electrospun fibers for the OER in water electrolysis. Therefore, a valuable basis for subsequent experimental work is ensured with promising perspectives for the obtention of a catalyst with a higher activity.

Appendix Experimental Setup and Procedure

Electrospinning Protocol

• Fill syringe with solution (either with cannula or through electrospinner tip)

• Set syringe pumps: v = 1.2 mL/h, d = 15.8 mm; then start pump (Place watch glass underneath, run to prevent drying out).

- Distance between collector and electrospinner tip (approx. 12.5 cm)
- Cover plate collector with aluminium foil
- Align microscope to tip, check on laptop.
- Switch on the fume hood at the top rear.
- Check grounding cable on collector
- Switch on Humidity Control [ON]: 33 %RH; wait until desired humidity is reached.
- Connect tips to high voltage source (red cables)
- Set the high voltage (15 kV for one tip)
- Close the hood

Switch on the high voltage [ON] (electrospinning starts here!) (Volume that has already through the syringe = V0)

- After the desired running time, switch off the high voltage [OFF].
- Wait 5 min until potentials are reduced!
- Switch off Humidity-Control and rotating collector [OFF]
- Open hood

• Before touching the syringe / tip: Short-circuit the tip and ground (this ensures that there is no residual potential).

• Remove syringe with needle from the electrospinner, return excess solution to storage container, wash needle and tip with water and dry with compressed air.

• Wash storage container, needle and tip with water or solvent and dry with compressed air.

• Remove the aluminum foil with the product from the collector and scrape off the product with a plastic spatula and weigh it

Detailed synthesis of the MOF-74

LG01 (Ni₅₀Co₅₀DOT)

2,5-Dihydroxyterephthalic acid (3.13 g, 15.82 mmol, 1 eq.) was dissolved in a solvent-mixture of DMF:EtOH:H2O 50:3:3 (560 mL). Nickel acetate (1.97 g, 7.91 mmol, 1 eq.) and cobalt acetate (1.97 g, 7.91 mmol, 1 eq.) were added under stirring (500 rpm) and the solution was heated to 120 °C for 6 h under reflux. The solution was allowed to cool to 20 °C slowly and was stirred for 14 h. The suspension was filtered (PTFE filter 0.45 μ m) and suspended in DMF (100 mL), stirred for 1 h and filtered again. Then it was suspended in MeOH (100 mL) and stirred for 1 h. The suspension was filtered over a PES filter (0.8 μ m) and left on air for 20 h. Then it was activated in a vacuum of 3.8 x 10⁻³ mbar and the brown solid (2.65 g) was stored under argon.

LG02 (Ni75Co25DOT)

2,5-Dihydroxyterephthalic acid (3.13 g, 15.82 mmol, 1 eq.) was dissolved in a solvent-mixture of DMF:EtOH:H2O 50:3:3 (560 mL). Nickel acetate (2.95 g, 11.87 mmol, 0.75 eq.) and cobalt acetate (0.99 g, 3.96 mmol, 0.25 eq.) were added under stirring (500 rpm). The suspension was heated to 120 °C for 5 h under reflux. The solution was allowed to cool to 20 °C slowly under stirring for 14 h. The suspension was filtered (PTFE filter 0.45 μ m), suspended in DMF (100 mL), stirred for 1 h and filtered again. Then it was suspended in MeOH (100 mL) and stirred for 1 h. The suspension was filtered over a PES filter (0.8 μ m) and left on air for 20 h. Then it was activated in a vacuum of 4 x 10⁻³ mbar and the brown solid (3.32 g) was stored under argon.

LG03 (Ni25Co75DOT)

2,5-Dihydroxyterephthalic acid (3.13 g, 15.81 mmol, 1 eq.) was dissolved in a solvent-mixture of DMF:EtOH:H2O 50:3:3 (560 mL). Nickel acetate (0,98 g, 3.95 mmol, 0.25 eq.) and cobalt acetate (2.95 g, 11.86 mmol, 0.75 eq.) were added under stirring (500 rpm) and the solution was heated to 120 °C for 6 h under reflux. The solution was allowed to cool to 20 °C slowly and was stirred for 14 h. The suspension was filtered (PTFE filter 0.45 μ m), suspended in DMF (100 mL), stirred for 2.5 h and filtered again. Then it was suspended in MeOH (100 mL) and stirred for 1 h. The suspension was filtered over a PES filter (0.8 μ m) and left on air for 20 h. Then it was activated in a vacuum of 2.3 x 10⁻³ mbar and the brown solid (3.48 g) was stored under argon.

LG04 (CoDOT)

2,5-Dihydroxyterephthalic acid (3.13 g, 15.81 mmol, 1 eq.) was dissolved in a solvent-mixture of DMF:EtOH:H2O 50:3:3 (560 mL). Cobalt acetate (4.00 g, 15.81 mmol, 1 eq.) was added under stirring (500 rpm) and the solution was heated to 120 °C for 6 h under reflux. The solution was allowed to cool to 20 °C slowly and was stirred for 14 h. The suspension was filtered (PTFE filter 0.45 μ m), suspended in DMF (100 mL), stirred for 2.5 h and filtered again. Then it was suspended in MeOH (100 mL) and stirred for 1 h. The suspension was filtered over a PES filter (0.8 μ m) and left on air for 20 h. Then it was activated in a vacuum of 2.3 x 10⁻³ mbar and the brown solid (3.50 g) was stored under argon.

Appendix Results and discussion



In this Appendix, more results are included.

Figure 48: SEM images of electrospun fibers from a solution with 8 wt % of concentration of PVP and (a) Methanol, (b) Ethanol, (c) Ethanol/DMF 50/50 w/w, and of (d) PAN and DMF (10 K x of magnification).





(e) (f) Figure 49: SEM images of PAN fibers before pyrolyzation (left column) and after pyrolyzation (right column) at 40 K x (a and b), 10 K x (c and d) and 5 K x (e and f) of magnification







(b) Figure 50: TGA of PVP fibers under N2 atmosphere.



Figure 51: TGA Analysis of (a) Ni₇₅Co₂₅-MOF74, (b) Ni₅₀Co₅₀-MOF74, (c) Ni₂₅Co₇₅-MOF74 and (d) Co-MOF74





(c)





(d)



(i) (j) Figure 52: SEM images of the MOFs at 5 K of Magnification. Before pyrolyzation: left column; after pyrolyzation right column (a) and (b) Ni-MOF74; (c) and (d) Ni₇₅Co₂₅-MOF74; (e) and (f) Ni₅₀Co₅₀-MOF74; (g) and (h) Ni₂₅Co₇₅-MOF74; (i) and (j) Co-MOF74



(a)



(b)



(i) Figure 53: SEM images of the MOFs at 10 K of Magnification. Before pyrolyzation: left column; after pyrolyzation right column. (a) and (b) Ni-MOF74; (c) Ni₇₅Co₂₅-MOF74; (e) and (f) Ni₅₀Co₅₀-MOF74; (g) and (h) Ni₂₅Co₇₅-MOF74; (i) and (j) Co-MOF74







(i) Figure 54: SEM images of the MOFs at 50 K of Magnification. Before pyrolyzation: left column; after pyrolyzation right column. (a) and (b) Ni-MOF74; (c) and (d) Ni₇₅Co₂₅-MOF74; (f) Ni₅₀Co₅₀-MOF74; (g) and (h) Ni₂₅Co₇₅-MOF74; (i) and (j) Co-MOF74





(a) (b) Figure 55: EDS analysis of PAN+Ni-MOF74. SEM and overlapped image of SEM and Ni distribution map of the same region. (5 K x of Magnification)



Figure 56: Single element images at 5 K x of Magnification from the EDS mapping of the combined catalyst PAN+Ni-MOF74

PANgc04 01_a - AB3 - SE - 20kV - 50000x

EDS-Schichtbild - PANgc04 01_a - AB3 - 20kV - 50000x





(a) (b) Figure 57: EDS analysis of PAN+Ni-MOF74. SEM and overlapped image of C and Ni distribution map of the same region. (50 K x of Magnification)



Figure 58: Single element images at 50 K x of Magnification from the EDS mapping of the combined catalyst PAN+Ni-MOF74.

References

- Rao AB, Rubin ES. A technical, economic, and environmental assessment of amine-based CO2 capture technology for power plant greenhouse gas control. Environmental science & technology 2002;36(20):4467–75.
- [2] Jackson R, Friedlingstein P., Canadell J. G., Andrew R. Two or three degrees: CO2 emissions and global temperature impacts. The Bridge 2015;45(2):16–21.
- [3] Züttel A. Hydrogen storage and distribution systems. Mitig Adapt Strat Glob Change 2007;12(3):343-65.
- [4] Christopher K, Dimitrios R. A review on exergy comparison of hydrogen production methods from renewable energy sources. Energy Environ. Sci. 2012;5(5):6640.
- [5] Cho MK, Lim A, Lee SY, Kim H-J, Yoo SJ, Sung Y-E et al. A Review on Membranes and Catalysts for Anion Exchange Membrane Water Electrolysis Single Cells. J. Electrochem. Sci. Technol 2017;8(3):183–96.
- [6] Zeng K, Zhang D. Recent progress in alkaline water electrolysis for hydrogen production and applications. Progress in Energy and Combustion Science 2010;36(3):307–26.
- [7] Holladay JD, Hu J, King DL, Wang Y. An overview of hydrogen production technologies. Catalysis Today 2009;139(4):244–60.
- [8] P. Millet. Int. J. Hydrogen Energy 1996;21, 87–93.
- [9] Goñi-Urtiaga A, Presvytes D, Scott K. Solid acids as electrolyte materials for proton exchange membrane (PEM) electrolysis: Review. International Journal of Hydrogen Energy 2012;37(4):3358–72.
- [10] K. Ito. Hydrogen Energy Engineering: Water Electrolysis 2016:p.143–149Polymer Electrolyte Membrane.
- [11] Leng Y, Chen G, Mendoza AJ, Tighe TB, Hickner MA, Wang C-Y. Solid-state water electrolysis with an alkaline membrane. Journal of the American Chemical Society 2012;134(22):9054–7.
- [12] Puthiyapura VK, Pasupathi S, Su H, Liu X, Pollet B, Scott K. Investigation of supported IrO2 as electrocatalyst for the oxygen evolution reaction in proton exchange membrane water electrolyser. International Journal of Hydrogen Energy 2014;39(5):1905–13.
- [13] Thangavel P, Ha M, Kumaraguru S, Meena A, Singh AN, Harzandi AM et al. Graphenenanoplatelets-supported NiFe-MOF: high-efficiency and ultra-stable oxygen electrodes for sustained alkaline anion exchange membrane water electrolysis. Energy Environ. Sci. 2020;13(10):3447–58.
- [14] Dou Y, Zhang W, Kaiser A. Electrospinning of Metal-Organic Frameworks for Energy and Environmental Applications. Advanced science (Weinheim, Baden-Wurttemberg, Germany) 2020;7(3):1902590.
- [15] Hamann CH, Vielstich W. Elektrochemie. 4th ed. Weinheim: Wiley-VCH-Verlag GmbH &Co. KGaA; 2005.
- [16] Ciribelli BN, Colmati F, Souza EC de. Nernst equation applied to electrochemical systems and centenary of his Nobel Prize in chemistry. IJIER 2020;8(11):670–83.
- [17] Rodríguez J, Amores E. CFD Modeling and Experimental Validation of an Alkaline Water Electrolysis Cell for Hydrogen Production. Processes 2020;8(12):1634.
- [18] Ahmad Kamaroddin MF, Sabli N, Tuan Abdullah TA, Siajam SI, Abdullah LC, Abdul Jalil A et al. Membrane-Based Electrolysis for Hydrogen Production: A Review. Membranes 2021;11(11).

- [19] Barelli L, Bidini G, Cinti G. Airflow Management in Solid Oxide Electrolyzer (SOE) Operation: Performance Analysis. ChemEngineering 2017;1(2):13.
- [20] Miller HA, Bouzek K, Hnat J, Loos S, Bernäcker CI, Weißgärber T et al. Green hydrogen from anion exchange membrane water electrolysis: a review of recent developments in critical materials and operating conditions. Sustainable Energy Fuels 2020;4(5):2114–33.
- [21] Li C, Baek J-B. The promise of hydrogen production from alkaline anion exchange membrane electrolyzers. Nano Energy 2021;87:106162.
- [22] Chi J, Yu H. Water electrolysis based on renewable energy for hydrogen production. Chinese Journal of Catalysis 2018;39(3):390–4.
- [23] Escorihuela J, García-Bernabé A, Montero Á, Sahuquillo Ó, Giménez E, Compañ V. Ionic Liquid Composite Polybenzimidazol Membranes for High Temperature PEMFC Applications. Polymers 2019;11(4).
- [24] Park JE, Kang SY, Oh S-H, Kim JK, Lim MS, Ahn C-Y et al. High-performance anion-exchange membrane water electrolysis. Electrochimica Acta 2019;295:99–106.
- [25] Shiva Kumar S, Himabindu V. Hydrogen production by PEM water electrolysis A review. Materials Science for Energy Technologies 2019;2(3):442–54.
- [26] Wang X, Xiao H, Li A, Li Z, Liu S, Zhang Q et al. Constructing NiCo/Fe3O4 Heteroparticles within MOF-74 for Efficient Oxygen Evolution Reactions. Journal of the American Chemical Society 2018;140(45):15336–41.
- [27] Britt D, Furukawa H, Wang B, Glover TG, Yaghi OM. Highly efficient separation of carbon dioxide by a metal-organic framework replete with open metal sites. Proceedings of the National Academy of Sciences of the United States of America 2009;106(49):20637–40.
- [28] Cadot S, Veyre L, Luneau D, Farrusseng D, Alessandra Quadrelli E. A water-based and high spacetime yield synthetic route to MOF Ni 2 (dhtp) and its linker 2,5-dihydroxyterephthalic acid. J. Mater. Chem. A 2014;2(42):17757–63.
- [29] Férey G. Hybrid porous solids: past, present, future. Chemical Society reviews 2008;37(1):191– 214.
- [30] Wang LJ, Deng H, Furukawa H, Gándara F, Cordova KE, Peri D et al. Synthesis and characterization of metal-organic framework-74 containing 2, 4, 6, 8, and 10 different metals. Inorganic chemistry 2014;53(12):5881–3.
- [31] Ma TY, Dai S, Jaroniec M, Qiao SZ. Metal-organic framework derived hybrid Co3O4-carbon porous nanowire arrays as reversible oxygen evolution electrodes. Journal of the American Chemical Society 2014;136(39):13925–31.
- [32] Dou Y, Zhang W, Kaiser A. Electrospinning of Metal-Organic Frameworks for Energy and Environmental Applications. Advanced science (Weinheim, Baden-Wurttemberg, Germany) 2020;7(3):1902590.
- [33] Reneker DH, Yarin AL, Fong H, Koombhongse S. Bending instability of electrically charged liquid jets of polymer solutions in electrospinning. Journal of Applied Physics 2000;87(9):4531–47.
- [34] Coles SR, Wooldridge A. Electrospinning: Principles, Practice and Possibilities: Chapter 4. Optimising Solutions for Electrospinning: The Royal Society of Chemistry; 2015.
- [35] Fong H, Chun I, Reneker D. Beaded nanofibers formed during electrospinning. Polymer 1999;40(16):4585–92.
- [36] Demetrius S. Gomes, Ana N. R. da Silva, Nilton I. Morimoto, Luiz T. F. Mendes, Rogerio Furlan, Idalia Ramos, Gomes DS, Da Silva ANR, Morimoto NI, Mendes LTF, Furlan R et al. Characterization

of an electrospinning process using different PAN/DMF concentrations. Polímeros 2007;17(3):206–11.

- [37] Huang Z-M, Zhang Y-Z, Kotaki M, Ramakrishna S. A review on polymer nanofibers by electrospinning and their applications in nanocomposites. Composites Science and Technology 2003;63(15):2223–53.
- [38] Edwards MD, Mitchell GR, Mohan SD, Olley RH. Development of orientation during electrospinning of fibres of poly(ε-caprolactone). European Polymer Journal 2010;46(6):1175– 83.
- [39] Utkarsh, Hegab H, Tariq M, Syed NA, Rizvi G, Pop-Iliev R. Towards Analysis and Optimization of Electrospun PVP (Polyvinylpyrrolidone) Nanofibers. Advances in Polymer Technology 2020;2020:1–9.
- [40] Kchaou M, Alquraish M, Abuhasel K, Abdullah A, Ali AA. Electrospun Nanofibrous Scaffolds: Review of Current Progress in the Properties and Manufacturing Process, and Possible Applications for COVID-19. Polymers 2021;13(6).
- [41] Davis FJ, Mohan SD, Ibraheem MA. Electrospinning: Principles, Practice and Possibilities: Chapter 1. Introduction: The Royal Society of Chemistry; 2015.
- [42] Yang Q, Li Z, Hong Y, Zhao Y, Qiu S, Wang C et al. Influence of solvents on the formation of ultrathin uniform poly(vinyl pyrrolidone) nanofibers with electrospinning. J. Polym. Sci. B Polym. Phys. 2004;42(20):3721–6.
- [43] Thompson CJ, Chase GG, Yarin AL, Reneker DH. Effects of parameters on nanofiber diameter determined from electrospinning model. Polymer 2007;48(23):6913–22.
- [44] Zhang C, Yuan X, Wu L, Han Y, Sheng J. Study on morphology of electrospun poly(vinyl alcohol) mats. European Polymer Journal 2005;41(3):423–32.
- [45] Yuan X, Zhang Y, Dong C, Sheng J. Morphology of ultrafine polysulfone fibers prepared by electrospinning. Polym. Int. 2004;53(11):1704–10.
- [46] Zhao S, Wu X, Wang L, Huang Y. Electrospinning of ethyl-cyanoethyl cellulose/tetrahydrofuran solutions. J. Appl. Polym. Sci. 2004;91(1):242–6.
- [47] Bhardwaj N, Kundu SC. Electrospinning: a fascinating fiber fabrication technique. Biotechnology advances 2010;28(3):325–47.
- [48] Rose M, Böhringer B, Jolly M, Fischer R, Kaskel S. MOF Processing by Electrospinning for Functional Textiles. Adv. Eng. Mater. 2011;13(4):356–60.
- [49] Lai Q, Zhao Y, Liang Y, He J, Chen J. In Situ Confinement Pyrolysis Transformation of ZIF-8 to Nitrogen-Enriched Meso-Microporous Carbon Frameworks for Oxygen Reduction. Adv. Funct. Mater. 2016;26(45):8334–44.
- [50] McCarthy DL, Liu J, Dwyer DB, Troiano JL, Boyer SM, DeCoste JB et al. Electrospun metal–organic framework polymer composites for the catalytic degradation of methyl paraoxon. New J. Chem. 2017;41(17):8748–53.
- [51] Chuangchote S, Sagawa T, Yoshikawa S. Electrospinning of poly(vinyl pyrrolidone): Effects of solvents on electrospinnability for the fabrication of poly(p -phenylene vinylene) and TiO 2 nanofibers. J. Appl. Polym. Sci. 2009;114(5):2777–91.
- [52] Nakhaei O, Shahtahmassebi N, Rezaee Roknabadi M, Behdani M. Fabrication and study of UVshielding and photocatalytic performance of uniform TiO2/SiO2 core-shell nanofibers via singlenozzle co-electrospinning and interface sol–gel reaction. Scientia Iranica 2016;23(6):3135–44.

- [53] Ji D, Peng S, Fan L, Li L, Qin X, Ramakrishna S. Thin MoS 2 nanosheets grafted MOFs-derived porous Co–N–C flakes grown on electrospun carbon nanofibers as self-supported bifunctional catalysts for overall water splitting. J. Mater. Chem. A 2017;5(45):23898–908.
- [54] Rahaman M, Ismail AF, Mustafa A. A review of heat treatment on polyacrylonitrile fiber. Polymer Degradation and Stability 2007;92(8):1421–32.
- [55] Xiao S, Lv H, Tong Y, Xu L, Chen B. Thermal behavior and kinetics during the stabilization of polyacrylonitrile precursor in inert gas. J. Appl. Polym. Sci. 2011;122(1):480–8.
- [56] Konstantopoulos G, Soulis S, Dragatogiannis D, Charitidis C. Introduction of a Methodology to Enhance the Stabilization Process of PAN Fibers by Modeling and Advanced Characterization. Materials (Basel, Switzerland) 2020;13(12).
- [57] Joseph I. Goldstein, Dale E. Newbury, Joseph R. Michael, Nicholas W.M. Ritchie, John Henry J. Scott, David C. Joy (ed.). Scanning Electron Microscopy and X-Ray Microanalysis.
- [58] Charles B. Boss and Kenneth J. Fredeen. Concepts, Instrumentation and Techniques in Inductively Coupled Plasma Optical Emission Spectrometry: Perkin Elmer.
- [59] Thermo Fisher Scientific. ICP-OES Sample Preparation; Available from: https://www.thermofisher.com/de/de/home/industrial/spectroscopy-elemental-isotopeanalysis/spectroscopy-elemental-isotope-analysis-learning-center/trace-elemental-analysistea-information/icp-oes-information/icp-oes-sample-preparation.html.
- [60] Elgrishi N, Rountree KJ, McCarthy BD, Rountree ES, Eisenhart TT, Dempsey JL. A Practical Beginner's Guide to Cyclic Voltammetry. J. Chem. Educ. 2018;95(2):197–206.
- [61] Everett DH. Manual of Symbols and Terminology for Physicochemical Quantities and Units, Appendix II: Definitions, Terminology and Symbols in Colloid and Surface Chemistry. Pure and Applied Chemistry 1972;31(4):577–638.
- [62] Palchoudhury S, Baalousha M, Lead JR. Methods for Measuring Concentration (Mass, Surface Area and Number) of Nanomaterials;8:153–81.
- [63] Quantachrome Instruments. Operating Manual 77–82; Available from: Quantachrome Instruments. Operating Manual 2008, 77–82.
- [64] Patrick Elsäßer. Porous M-N-C electrocatalysts for the oxygen reduction reaction,. Bachelorarbeit. Freiburg im Breisgau; 2015.
- [65] Melke J, Martin J, Bruns M, Hügenell P, Schökel A, Montoya Isaza S et al. Investigating the Effect of Microstructure and Surface Functionalization of Mesoporous N-Doped Carbons on V 4+ /V 5+ Kinetics. ACS Appl. Energy Mater. 2020;3(12):11627–40.
- [66] Walker EE. The solvent action of organic substances on polyacrylonitrile. Journal of Applied Chemistry 1952.
- [67] Kobayashi S, Müllen K. Encyclopedia of Polymeric Nanomaterials. Berlin, Heidelberg: Springer Berlin Heidelberg; 2015.
- [68] O'Neil, M.J. (ed.). The Merck Index An Encyclopedia of Chemicals, Drugs, and Biologicals. Cambridge, UK: Royal Society of Chemistry, 2013., p. 1106.
- [69] Hieu NT, Suk J, Kim DW, Park JS, Kang Y. Electrospun nanofibers with a core-shell structure of silicon nanoparticles and carbon nanotubes in carbon for use as lithium-ion battery anodes. J. Mater. Chem. A 2014;2(36):15094–101.
- [70] Alibe I, Matori A, Saion E, Ali A, Zaid M. The influence of calcination temperature on structural and optical properties of ZnO nanoparticles via simple polymer synthesis route. Sci Sintering 2017;49(3):263–75.

- [71] Loría-Bastarrachea MI, Herrera-Kao W, Cauich-Rodríguez JV, Cervantes-Uc JM, Vázquez-Torres H, Ávila-Ortega A. A TG/FTIR study on the thermal degradation of poly(vinyl pyrrolidone). J Therm Anal Calorim 2011;104(2):737–42.
- [72] Bipul Barua. INVESTIGATION OF ELECTROSPINNING PROCESS PARAMETERS AND STUDIES OF STABILIZATION KINETICS OF POLYACRYLONITRILE-BASED ELECTROSPUN CARBON NANOFIBERS; 2015.