Westfälische Hochschule

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DEVELOPMENT OF CATALYST MATERIALS BASED ON CARBON NANOFIBERS FOR ELECTROCHEMICAL CELL APPLICATIONS

Summary of the PhD Thesis
submitted to obtain the scientific title of
Doctor Engineer
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in the field of CHEMICAL ENGINEERING
for
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Contents

ABBREVIATIONS

b	Tafel Slope
CB	Carbon Black
CNF	Carbon Nanofiber
CV	Cyclic Voltammetry
d.c	Duty Cycle
$E°$	Standard Electrode Potential
E_{corr}	Corrosion Potential
ECSA	Electrochemical Active Surface Area
EDX	Energy Dispersive X-Ray Spectroscopy
GANF	Grupo Antolin Nanofibers
GDL	Gas Diffusion Layer
HER	Hydrogen Evolution Reaction
HOR	Hydrogen Oxidation Reaction
i	Current Density
i_{corr}	Corrosion Current Density
i_o	Exchange Current Density
LSV	Linear Scan Voltammetry
MEA	Membrane Electrode Assembly
OCP	Open Circuit Potential
OCV	Open Circuit Voltage
OER	Oxygen Evolution Reaction
ORR	Oxygen Reduction Reaction
PCD	Pulsed Current Deposition
PEMFC	Polymer Electrode Membrane Fuel Cell
SCE	Saturated Calomel Electrode
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analysis
t_{on}	Time when deposition potential/current density is applied
t_{off}	Time during no current flow is applied
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence Spectroscopy
α	Charge Transfer Coefficient

1. Introduction and aim of the work

Building a sustainable future has lately become a priority. The economic development during the last period led to discovery of new energy sources as well as new viable alternatives for replacing the fossil fuels as coal, oil and natural gas [1], which are finite, non-renewable and have a negative impact on the environment. These facts, correlated with the increase of world population and demand, thrust into the necessity of finding alternative energy sources. On the other hand, it is necessary to defeat the environmental issues, which are associated with the use of conventional sources above mentioned. CO_2 emissions that result from fossil fuel combustion are known to cause the “greenhouse effect” which is the main reason for global warming. From this point of view, eco-friendly technologies are demanded, that can produce constant energy, without affecting the environment [2].

Recently, due to the great concern and intensive studies, several types of clean and renewable energy technologies have entered markets. It is expected that in a short time, the classic energy sources that produce undesired emissions will be slowly replaced by the new revolutionary clean sources [3]. A large variety of renewable resources are nowadays used for energy production as sunlight, wind, geothermal heat or biomass. Among these alternative energy suppliers, fuel cells can provide an important contribution to the global energy consumption, since it can reduce our dependence on fossil fuels and can be used in various applications from portable power to transport and stationary systems [4].

Fuel cells consist of an anode and a cathode which are separated by an electrolyte. Several types of fuel cells have been developed due to the differences in applications, operation mode, electrolyte material or membrane involved in the process [5]. A major current disadvantage of this technology is the high cost of the catalysts which are involved into the fuel cells production. Up to now, important progress has been realized in this field to reduce the production costs and to increase the efficiency. Other fundamental problems encountered in fuel cells production and employment are represented by the slow reaction rates as well as the fact that hydrogen is not an available fuel on the market [2]. Most of the actual hydrogen production employs fossil fuels both for energy and source. Water electrolysis is considered a promising option for a clean hydrogen production using renewable sources [6]. This process is based on splitting the water molecules into hydrogen and oxygen using electricity.

The great interest in developing clean technology for energy production brought remarkable progress in this field. Moreover, the promising role of fuel cells in providing clean energy has been proven within a great variety of studies.

In the actual state of the art, platinum is considered the most effective catalyst material for electrochemical reactions, but due to its prohibitive price, the use of this metal in industrial purposes is limited. Therefore, during last years, several materials have been investigated, in order to obtain efficient catalyst materials for electrochemical systems. Lately, scientists have endeavoured to reduce the platinum amount without affecting the desired characteristics like catalytic activity, structural stability, high electrical conductivity and good corrosion resistance.

Carbon based materials such as carbon nanofibers are suitable support materials for catalyst particles, providing an increased surface area, good mechanical properties, high electrical conductivity and nevertheless, good interaction with platinum particles. The high graphitization degree of the fibers provides a good corrosion resistance and assures a defect free crystalline material.

The **main goal** of the present study was to develop catalyst materials with high catalytic activity for electrochemical cell applications, based on carbon nanofibers decorated with platinum and platinum cobalt alloy particles.

The present thesis has been structured into 5 chapters:

Chapter 1 presents a short introduction, highlighting the background and motivation of the chosen topic.

Chapter 2 deals with state of the art in the field of catalysts, succinctly presenting some theoretical aspects regarding catalysts production, current fabrication methods, classification and main applications. Moreover, a brief description of the PEMFC technology is realized, emphasizing the key components and reaction mechanisms that appear during operation.

Chapter 3 describes the methodology and equipment used to accomplish the experimental program. This chapter offers an overview regarding the applied investigation methods and presents different analytic techniques which can provide important information on quality and performance of the developed catalyst materials.

Chapter 4 presents the experimental program concerning the functionalization treatment of the carbon support material, catalyst material deposition, reporting the detailed followed steps in order to obtain the catalyst electrodes and furthermore exhibits the results attained during this study, highlighting the important aspects.

Chapter 5 reveals the conclusions of this study and the original contributions achieved through this work.

2. Experimental program

The original contributions of the present study refer to the possibility of combining the **oxygen plasma functionalization treatment** of the support material (CNF with high graphitization degree) with the **electrochemical deposition method** (pulsed current deposition) to develop low **platinum** and **platinum-cobalt** loading catalysts, suitable for electrochemical devices, like fuel cells or water splitting electrolysers. In this regard, investigations on the degradation mechanism (corrosion resistance, thermal stability, graphitization degree) of the CNF support material after the functionalization treatment are performed. Studies on the deposition mechanisms of platinum and platinum-cobalt codeposition respectively from a self-developed electrolyte are accomplished by analysing the linear and cyclic polarisation curves carried out onto the support material. Moreover, the evaluation of the catalytic effect of the developed electrodes by determination of kinetic parameters for **HER** and **OER** respectively is realised in a three-electrode cell from acid and alkaline solutions. The performance of the electrodes as catalyst for **PEMFC** was verified in a single-cell test bench at room temperature.

Carbon-supported Pt nanoparticles are used in different fields, but one of the most important applications is as electrocatalyst for fuel cells. Several studies during the last years have revealed that there is a strong correlation between size and distribution of the catalyst particles on the surface of support material and the efficiency of the catalyst.

CNF with an increased specific surface area ($>100\ m^2\ g^{-1}$) and a high graphitization degree (≈100 %) were used as support material for catalyst particles deposition. The attention was focused on the improvement of handling and wettability of CNF, by subjecting them to a functionalization process. CNF have been treated in oxygen plasma and during this step, functional acidic groups were generated onto their surface. The advantages of this method are various. Through this treatment, different oxygen containing functional groups (carboxylic, carbonylic and hydroxylic) are generated on the outer surface of CNF, enhancing their dispersibility in a polar solvent. The presence of such functional groups leads also to considerable changes regarding the reactivity and improves considerably the catalyst deposition process. After the functionalization treatment, CNF were dispersed into isopropanol and the obtained ink was sprayed onto a gas diffusion layer. The obtained uncatalysed electrode represents the support material for platinum and platinum-cobalt particles which are subsequently deposited onto its surface. Figure 1 presents a schematic representation of the experimental program.

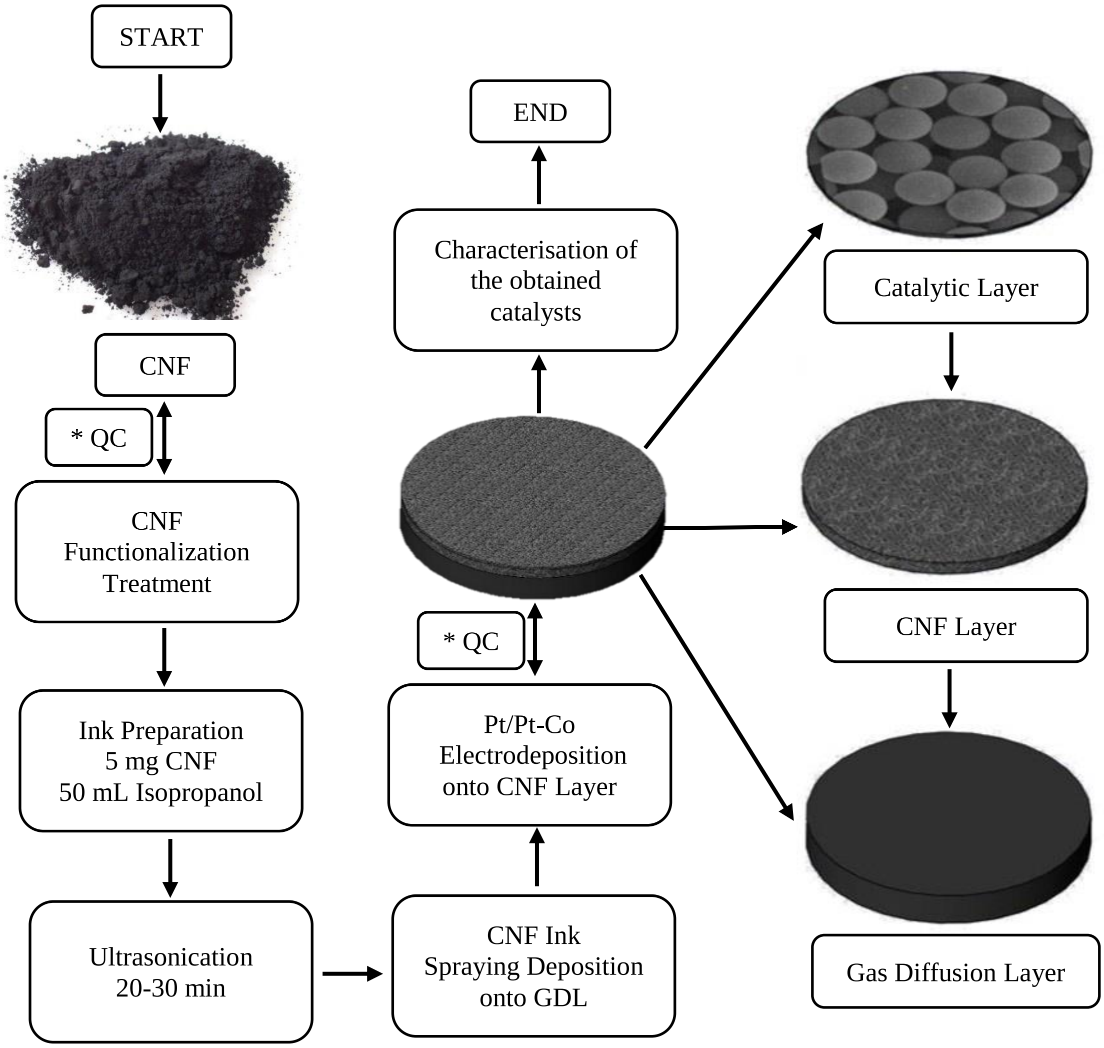

Figure 1. Schematic representation of the experimental program

Hence, CNF structures were subjected to plasma functionalisation treatment by applying three different sets of parameters which create onto the CNF surface a certain amount of functionalities. It is essential to determine the concentration of functional groups generated during the plasma treatment to establish the optimal treatment parameters that may lead to the desired functionalization degree of the CNF. After the plasma treatment, CNF were investigated in respect to the functionalization degree, particularly the concentration of functional groups attached to their surface. Nowadays, several investigation methods are available to determine the type of the functional groups, as well as their concentration. As the main groups created during the oxygen plasma treatment have been shown to possess an acidic character [7], a suitable method for estimation their concentration is an acid-base titration. Moreover, TGA investigations offer important information regarding the thermal stability, decomposition or combustion onset temperature of the structures and the effect of surface functionalization on the combustion temperature of CNF. Untreated CNF are thermally stable in the testing conditions below 650°C and no phase change can be observed. The combustion of CNF occurs once the 650°C temperature is reached, taking place in one single step and the maximum rate of combustion is achieved at 850°C.

Catalyst stability and durability is mainly influenced by the corrosion resistance of the support material. Electrochemical carbon corrosion is a major factor which contributes to performance mitigation during the fuel cell operation. Furthermore, the carbon degradation leads to significant loss of catalyst particles and consequently, a decrease of catalytic activity of the electrode occurs. Carbon black is more susceptible to corrosion than other carbon structures like CNF or CNT. Moreover, it has been shown that corrosion resistance of carbon is strongly related to the graphitic structure. An improved stability can be attributed to a lower amount of defect sites on the carbon surface, where the oxidation process occurs [8]. The corrosion resistance of the carbon structures depends on several parameters like specific surface area, surface composition, morphology or porosity [9]. The concentration of oxygen containing groups attached on the CNF outer surface during the plasma functionalization treatment plays an important role regarding the corrosion behaviour of CNF. Hydrophobicity of carbon surface is considered a significant factor, which improves the corrosion resistance of the material [10]. Defect sites created during functionalization treatment can corrode easily and may further cause and promote the oxidation. Functionalized samples exhibit slightly lower corrosion current density in comparison to the untreated fibers and this fact may be attributed to the presence of oxygen containing groups, which create a protective layer that can prevent the further oxidation of carbon. Moreover, the E_{corr} is shifted to more negative values, since the reactivity of the activated CNF increases. Smaller current density values were found for CNF 80 and CNF 100 samples, being correlated with a higher corrosion resistance of the material. In addition, the graphitization degree obtained from XRD measurements decreased from 99.6% to 78.8%. The smallest change in graphitization degree was observed for CNF 80 (94.8 %), value which is in good agreement with the corrosion resistance evaluation.

The catalyst deposition was carried out with the aid of a Potentiostat/Galvanostat Ivium Technologies Vertex in a three-electrode cell, with a SCE as reference and a platinum disk as counter electrode. The working electrode consisted in GDL samples cut in 15 mm diameter disks covered with CNF (Figure 2) without and with previous functionalization treatment, having an exposed surface are of 1 cm^2. The electrodeposition baths were developed by mixing K_2PtCl_4 as source for platinum ions, $CoCl_2$ as source for cobalt ions, KCl which assures an optimum electrical conductivity of the electrolyte and H_3BO_3 for stabilizing the pH value. The chemical composition of the deposition baths is presented in Table 1.

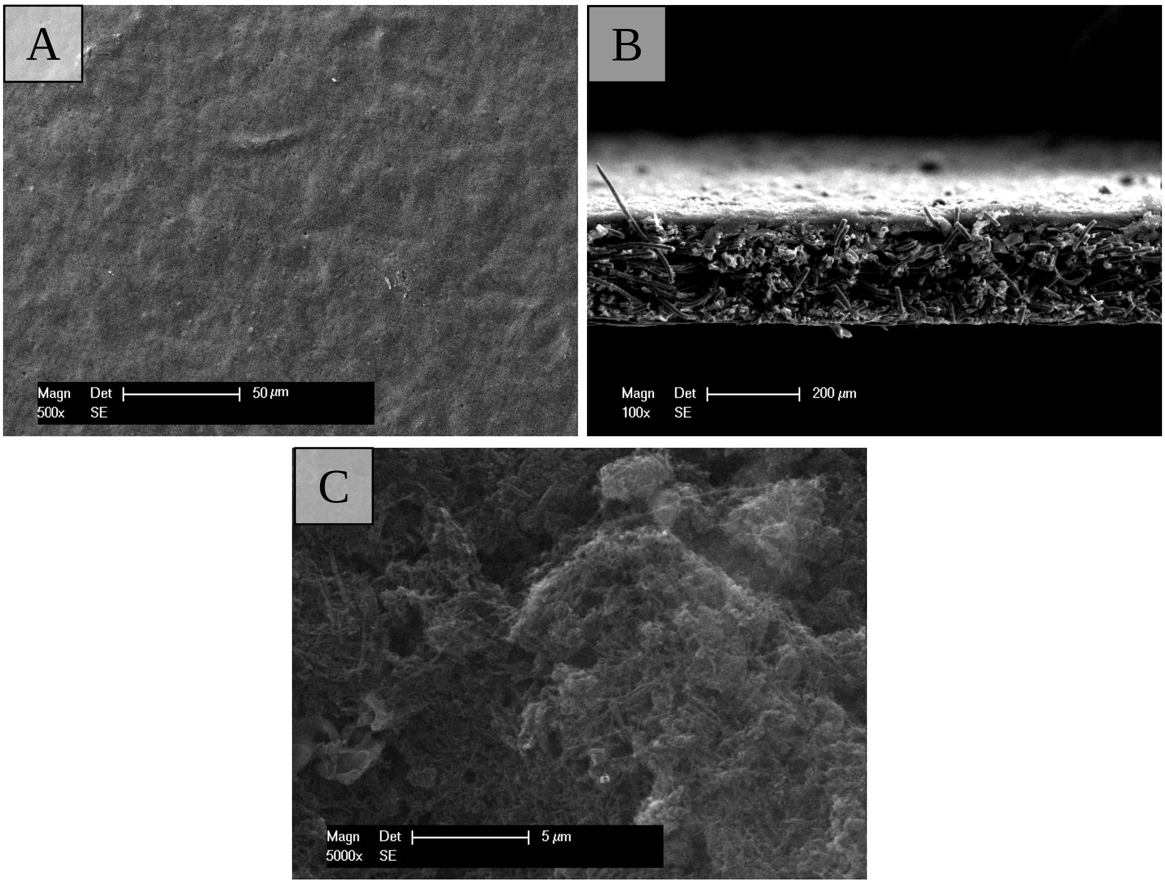

Figure 2. SEM micrographs of the GDL: A – surface; B – cross-section; C – GDL sprayed with CNF

Table 1. Chemical composition of platinum and cobalt electrolytes

Electrolyte	**K_2PtCl_4 [M]**	**$CoCl_2·6\,H_2O$ [M]**
Bath 1	0.005	-
Bath 2	-	0.1
Bath 3	0.005	0.0025
Bath 4	0.005	0.005
Bath 5	0.005	0.025
Bath 6	0.005	0.05
Bath 7	0.005	0.1

The platinum/cobalt deposition process takes place, according to *Eq. 1 – Eq. 2:*

$$PtCl_4^{2-} + 2e^- \rightarrow Pt + 4Cl^- \ (E^\circ = 0.605 \text{ V vs. SCE}) \qquad \text{Eq. 1}$$

$$Co^{2+} + 2e^- \rightarrow Co \ (E^\circ = -0.523 \text{ V vs. SCE}) \qquad \text{Eq. 2}$$

Concludent information is obtained from cyclic voltammograms (CV) (Figure 3) performed for Pt (Bath 1), Co (Bath 2) and Pt-Co alloy (Bath 3) deposition, with 5 mV s^{-1} scan rate, for 10 cycles. The presented plots represent the 10th cycle for each of the tested samples.

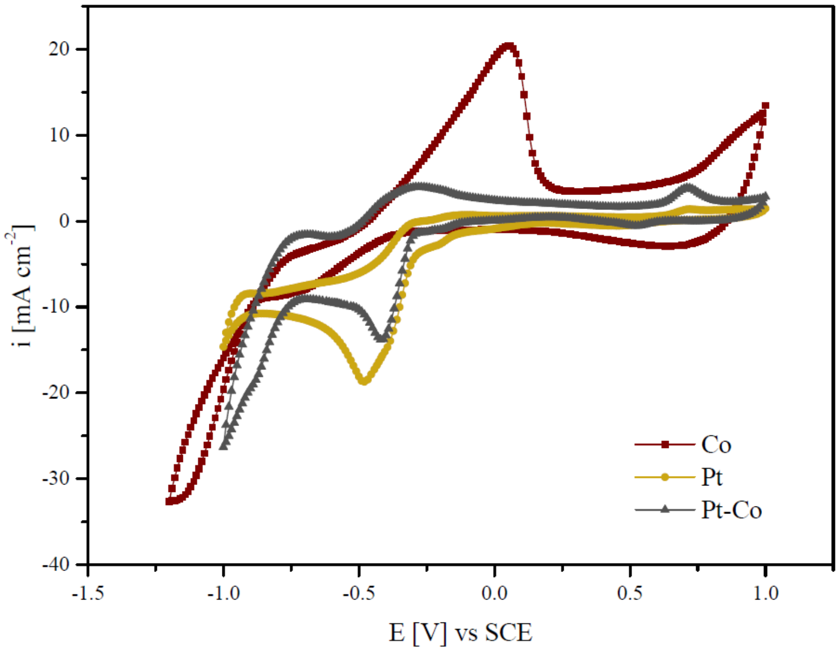

Figure 3. Cyclic voltammetry for Co, Pt and Pt-Co deposition process

The CV measurements provide important information regarding platinum and cobalt deposition mechanism from the investigated electrolytes, leading to a precise identification of the appropriate deposition parameters. During the cathodic polarization, around -0.5 V vs. SCE, the cobalt deposition process sets in with a low overpotential. As the current density increases, the nucleation process occurs, since it is related to the increase in density of the nuclei and crystal growth. At more pronounced cathodic polarization, HER occurs simultaneously with Co deposition (Co^{2+}/Co, $E° = -0.52$ V vs. SCE). Consequently, in the vicinity of the working electrode, the electrolyte solution is alkalized, and Co^{2+} cations can precipitate to $Co(OH)_2$. In these circumstances, Co deposition may occur through $Co(OH)_2$ reduction ($Co(OH)_2/Co$, $E° =$ -0.97 V vs. SCE) [11]. At anodic polarization, around -0.5 V vs. SCE, a high peak assigned to cobalt oxidation process can be observed. The same behaviour was previously reported by other studies [12]. The possibility of cobalt passivation can be as well taken into consideration, resulting species like CoOOH that come from CoOH or $Co(OH)_2$ which could have been previously adsorbed onto the electrode surface [13]. Over +0.75 V vs. SCE, the oxygen evolution reaction takes place, simultaneously with the cobalt dissolution.

Platinum deposition starts once the - 0.1 V vs. SCE potential is reached, towards the cathodic polarization. At more negative potentials, around -0.25 V vs. SCE, HER takes place simultaneously with the platinum reduction process. At -0.5 V vs. SCE, the current density is limited since the diffusion of Pt^{2+} ions from the bulk of the electrolyte solution to electrode becomes rate determining step. When the potential is scanned in the anodic direction, around +0.6 V vs. SCE, the current density slightly increases due to the platinum oxidation process.

For Pt and Co codeposition process, HER can be noticed in the cathodic region around 0.9 V vs. SCE, the reaction being catalysed by the freshly deposited platinum and cobalt particles. By scanning the potential in the cathodic direction, the current densities in the diffusion region are smaller in comparison with platinum deposition. The codeposition of Pt and Co is indicated by the presence of both cobalt oxidation peak, around -0.5 V vs. SCE and platinum oxidation around +0.6 V vs. SCE.

The catalyst deposition onto the CNF surface was performed applying a pulsed current technique from the electrolytes presented in Table 1. Schematic representation of *i-t* plots for platinum deposition process is presented in Figure 4.

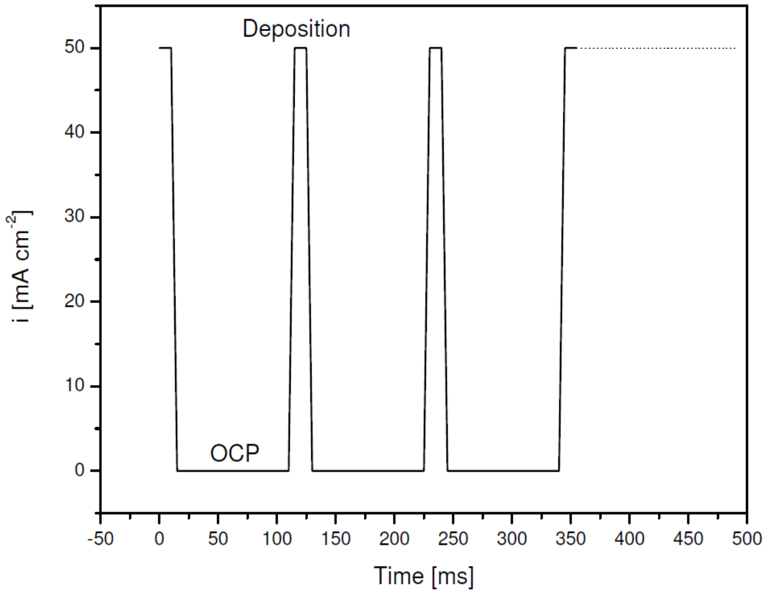

Figure 4. Schematic representation of *i-t* plots for platinum deposition process

The deposition parameters were adjusted to obtain a uniform distribution and reduced size catalyst particles on the CNF surface. The effect of several deposition parameters like current density, deposition time, duty cycle and number of cycles on the morphology of the obtained catalysts was also investigated.

The resulted CNF-Pt/Pt-Co electrodes with low platinum loading were further investigated by means of SEM combined with EDX, XRF, XRD and TGA to determine the morphology, chemical composition, distribution and amount of catalyst particles deposited onto the carbonic support material. The electrochemical surface area was determined by cyclic voltammetry in 0.5 M H_2SO_4 solution. SEM investigations revealed a homogeneous distribution of the catalyst particles with a nanometric size range for the samples prepared with a previous functionalization treatment of the CNF. A good distribution of catalyst particles onto the CNF support material is the main condition for attaining an improved electrocatalytic activity. Moreover, small particles are required to create a larger active surface area of the catalyst. Choosing the right deposition parameters, these conditions can be easily fulfilled. It is strongly necessary to correlate the modification of each deposition parameter with a rigorous control of the morphology quality.

A typical SEM micrograph of a Pt decorated CNF electrode, functionalized with 80 W is presented in Figure 5. The platinum particles agglomerated in nanoclusters are uniform located onto the CNF surface and the size distribution is constant. EDX spectrum confirms the presence of metallic platinum. Likewise, SEM micrograph of a Pt-Co/CNF electrode and the corresponding EDX spectrum is presented in Figure 6.

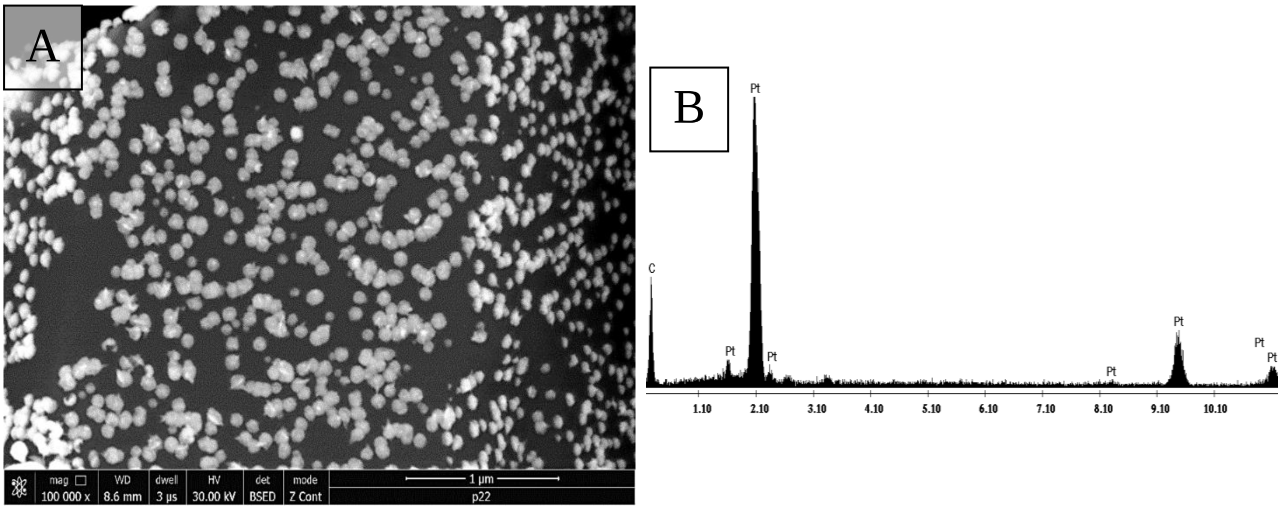

Figure 5. A – SEM micrograph of Pt/CNF electrode; B – EDX spectrum corresponding to the white spots

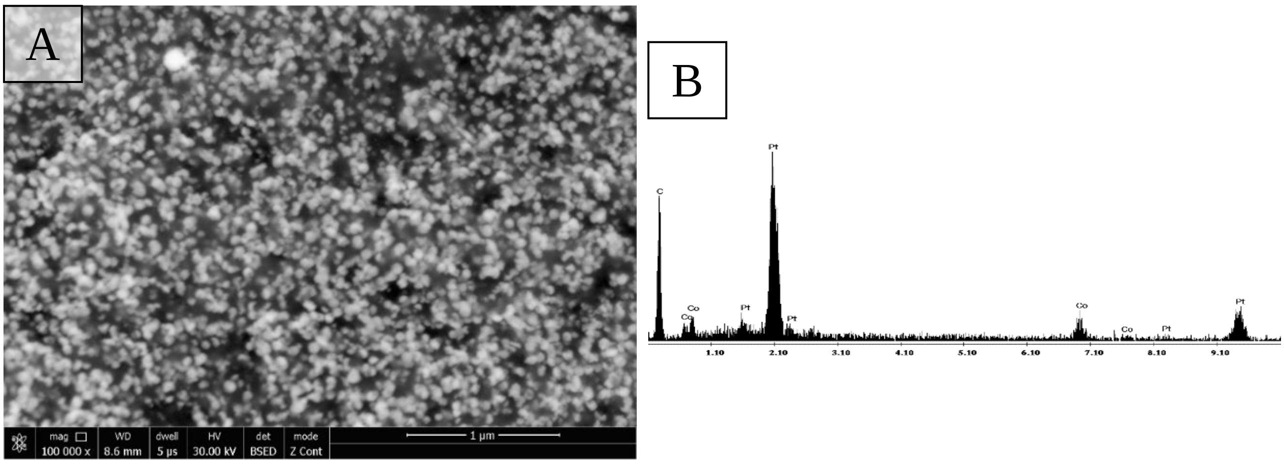

Figure 6. A – SEM micrograph of Pt-Co/CNF electrode; B – EDX spectrum corresponding to the white spots

Energy Dispersive X-Ray spectroscopy (EDX) mapping was used to collect the elemental composition and distribution and certain position of Pt and Co in the alloy structure. A representative EDX mapping is presented in Figure 7.

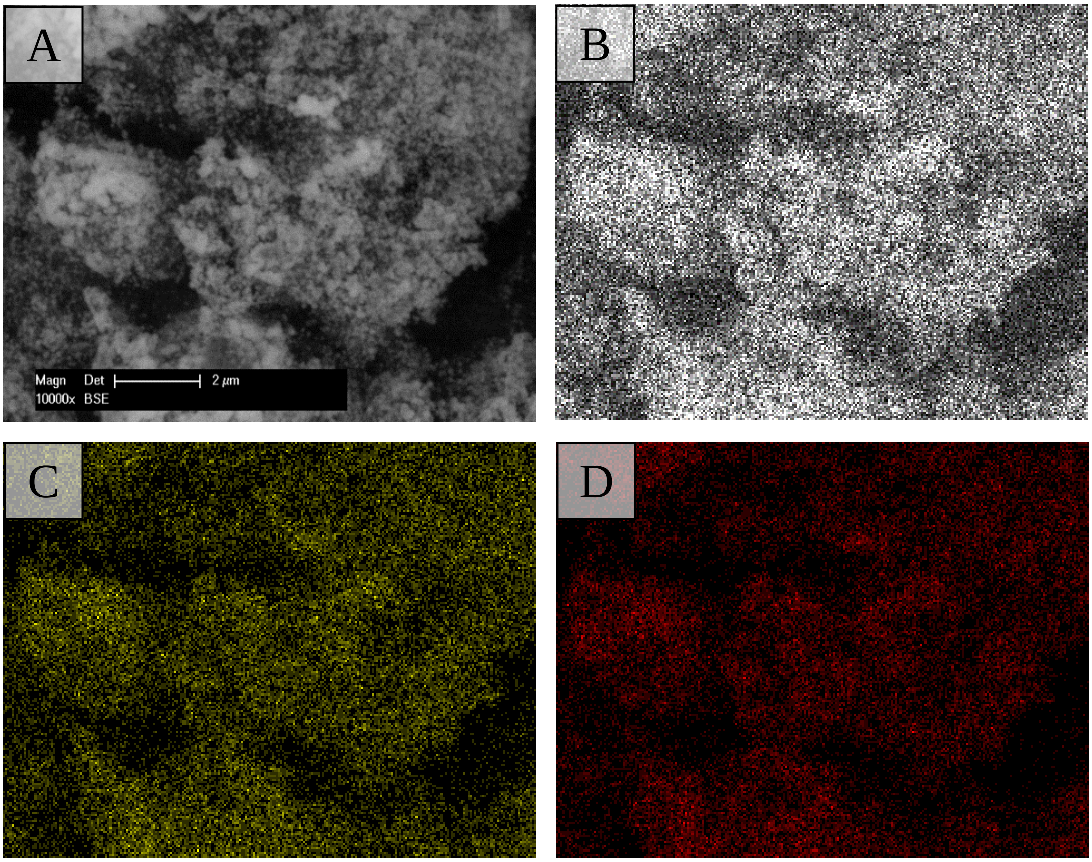

Figure 7. EDX mapping of the Pt-Co electrode obtained from Bath 6 (A-SEM micrograph; B-Pt-Co alloy; C-Pt; D-Co)

This investigation reveals a high alloying degree of the obtained Pt-Co catalyst. Both elements are evenly distributed throughout the electrode surface and platinum presents a higher content in comparison to cobalt.

Table 2 presents considerable higher ECSA for CNF 80 samples in comparison to untreated CNF supported catalysts. Due to the improved particles distribution achieved after functionalization treatment, observed in SEM micrographs correlated with a higher electrochemical surface area obtained for CNF 80 samples, one can affirm that by applying a plasma functionalization treatment (80 W for 1800 s), the ECSA and catalytic activity is significantly increased. Moreover, the particles size considerably decreased due to the intensification of nucleation process promoted by the presence of functionalization groups. Making an analogy with the crystallite sizes form XRD measurements, it can be affirmed that particle sizes obtained from ECSA method are larger. This can be attributed to the fact that platinum particles might be just partially electrochemical active and particles can be composed of more platinum crystallites agglomerated in a nanocluster.

Table 2. Pt loading, particle sizes and ECSA of the selected electrodes

Sample	**Pt loading [mg]**	**ECSA [m^2 g^{-1}]**	**Particle size[nm]**	
			ECSA	**XRD**
CNF untreated	0.157 ± 0.005	3.9 ± 0.3	72	41
CNF 80 W	0.185 ± 0.007	9.1 ±0.5	31	12
CNF 100 W	0.175 ± 0.003	6.8 ±0.1	41	21
CNF 120 W	0.167 ± 0.004	4.5 ±0.2	62	28

The optimized electrodes were further investigated by electrochemical means in order to analyse the catalytic activity regarding either the HER (Pt/CNF) or the OER (Pt-Co/CNF) in acid and alkaline mediums respectively. Moreover, the behaviour of the electrodes as electrocatalysts for fuel cells is analyzed performing in situ polarization curves in a PEMFC test bench at low temperatures.

The characteristics (structure, chemical composition and morphology) of the deposited catalyst particles have a strong influence especially on the catalytic activity over the electrode surface during operation in water splitting electrolyzers as well as fuel cells.

As it can be observed in Figure 8, the HER is significantly intensified and the onset potential decreases considerably for Pt/CNF functionalized samples. The HER depolarisation observed in the linear voltammetric plots is influenced by the amount of platinum onto the surface of the electrodes and by the ECSA consequently. Beyond the HER onset potential, the cathodic current densities are considerably higher for functionalized CNF based samples at the same overpotential value. Around -0.4 V/SCE, the cathodic current density for Pt/CNF 80 reaches much higher current densities than the untreated CNF samples. The enhanced HER activity can be attributed to the increased ECSA.

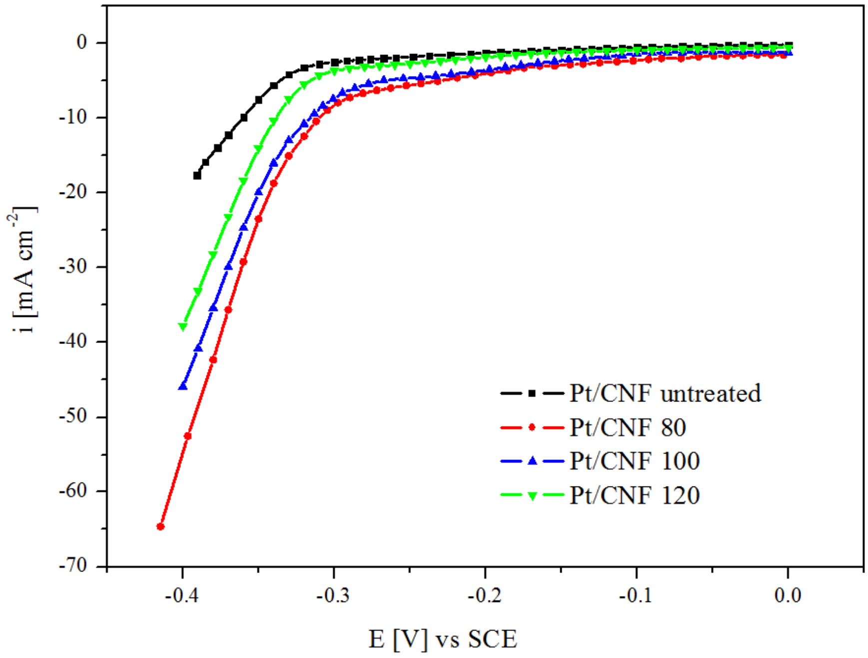

Figure 8. HER on selected Pt/CNF catalysts in 0.5 M H_2SO_4 solution

According to Table 3, the exchange current density increases considerably, more than 10 higher for samples prepared with plasma treated CNF compared to those prepared using untreated CNF as support. Additionally, comparing the exchange current densities of the treated CNF based samples, it can be observed that by applying a higher power during the functionalization treatment, a decrease in exchange current density values is obtained. The charge transfer coefficient, $1\text{-}\alpha$ slightly decreases from 0.57 for untreated CNF based electrodes to 0.44 for the sample functionalized with 80 W. As the $1\text{-}\alpha$ coefficient represents the fraction of the cathodic overpotential used for the enhancement of the electrode reaction, it can be stated the reaction plan is shifted to the electrolyte solution. This kinetically unfavourable effect is compensated by the exchange current density increase since the surface of CNF functionalized electrodes is more active in comparison to samples produced using untreated CNF. The exchange current density increase due to the high concentration of protons at the interface between electrode material and electrolyte [14].

Table 3. Tafel parameters for HER on untreated and treated CNF in 0.5 H_2SO_4

Sample	**b [mV dec^{-1}]**	**1-α**	**i_o [A m^{-2}]**
Pt/CNF untreated	103	0.57	0.13
Pt/CNF 80	135	0.44	1.88
Pt/CNF 100	105	0.56	1.22
Pt/CNF 120	129	0.46	0.26

Polarisation curves of prepared MEA have been plotted in a PEMFC test bench with using an electronic load type Höcherl & Hackl type ZS1806NV. U-i-plots are obtained in constant current mode and are presented in Figure 9. MEA were produced with the developed Pt/CNF electrodes, placed onto the anodic side of the cell where the HOR takes place.

It can be noticed that the open circuit voltage (OCV) for the investigated samples is higher than 1.0 V. The highest voltage drop appears at small current densities (0 – 200 mA cm^{-2} mg^{-1} Pt) and is associated to activation energy barrier of the electrochemical reactions. The activation polarization loss is higher for sample A1 in comparison to the other studied samples and can be linked to the smaller platinum amount found on this sample. Starting from 0.8 V, the voltage drops nearly linear with increasing load current, according to membrane and electrode resistance. The ohmic drop remains constant for all the investigated samples, since the support material and other significant factors are the same.

Experimental results show a maximum power density of around 400 mW cm^{-2} mg^{-1} Pt correlated with a developed current density of 800 mA cm^{-2} mg^{-1} Pt achieved at a practical voltage of 500 mV for anode A3, value comparable to other similar studies [15]. Electrodes A1 and A2 show inferior power and current density values due to the lower platinum loading found on their surface. The differences can be attributed to the current density value and number of cycles applied during the platinum electrodeposition process, parameters which can provide a higher catalyst amount and a better distribution when higher values are applied. The obtained power and current density values of the presented polarization curves are corrected with the platinum loading found on each of the investigated samples. It can be noticed that a higher platinum amount deposited onto the CNF support material leads to a 60 % increase in power output, improving the performance of the fuel cell. As the operation temperature inside the fuel cell is low, the gas diffusion and membrane conductivity is reduced, fact which is correlated with a decreased kinetic reaction, aspects which explain the lower current density values obtained for the studied samples in comparison to other reported studies.

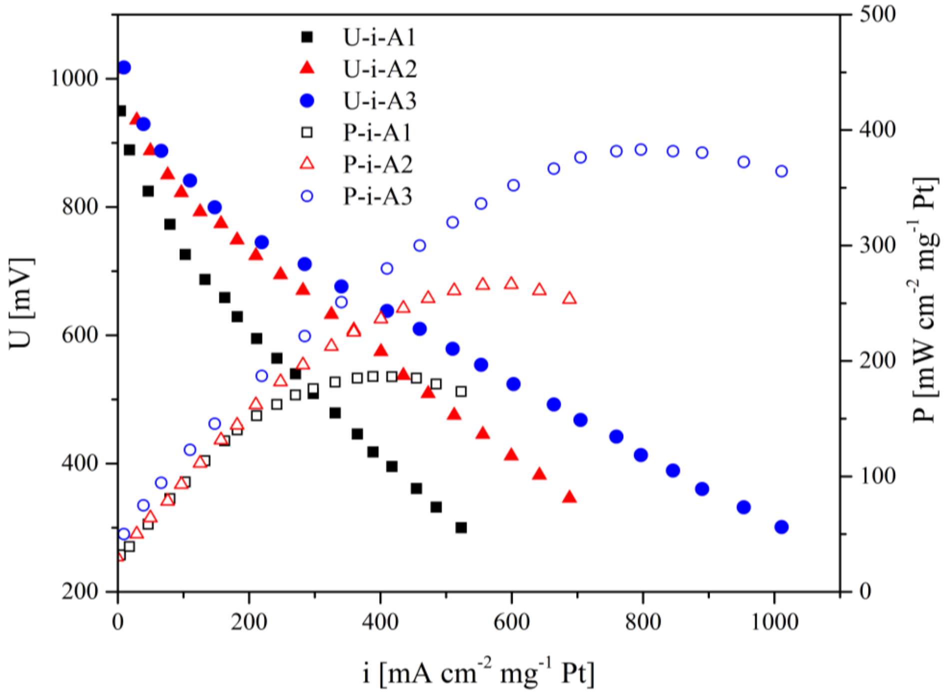

Figure 9. Polarization curves of MEA prepared with A1 – Pt/CNF 25 mA cm^{-2}, 10000 cycles, A2 - Pt/CNF 50 mA cm^{-2}, 5000 cycles; A3 - Pt/CNF 50 mA cm^{-2}, 10000 cycles

Table 4 presents the Pt-Co ratio in the deposited alloy structure, catalyst loading and *ECSA* values of the studied electrodes. Important differences in the chemical composition of Pt-Co /CNF samples as well as for the corresponding ECSA calculated from the CV polarisation curves can be observed. Although the Co concentration in the deposition electrolyte was higher than the Pt concentration (in all the studied cases), nobler metal (Pt) tends to deposit faster. This aspect explains the higher amount of platinum as well as the rich Pt alloy phase found on all the investigated samples. An increased *ECSA* is observed when a higher $CoPt_3$ alloy is formed.

Table 4. Pt-Co ratio, rest mass and ECSA of the Pt-Co electrodes

Sample	Pt-Co ratio [%]				Rest mass [mg]	*ECSA* [m^2 g^{-1}]	Particles size [nm]	
	XRF		**XRD**				**XRD**	**ECSA**
	Pt	Co	Pt	Co				
Pt-Co-1	72	28	88	12	0.28	2.1	50	130
Pt-Co-2	69	31	87	13	0.23	2.9	32	96
Pt-Co-3	65	35	85	15	0.21	8.6	13	32
Pt-Co-4	61	39	84	16	0.18	13.5	12	20
Pt-Co-5	62	38	86	14	0.2	9.6	19	30

The evaluation of the catalytic properties of the developed Pt-Co/CNF electrodes for OER is performed by linear sweep voltammetry in 1 M NaOH solution, by scanning the potential from 0 V vs. SCE to 0.7 V vs. SCE in the anodic direction with a scan rate of 5 mV s^{-1}. The obtained polarisation curves are shown in Figure 10.

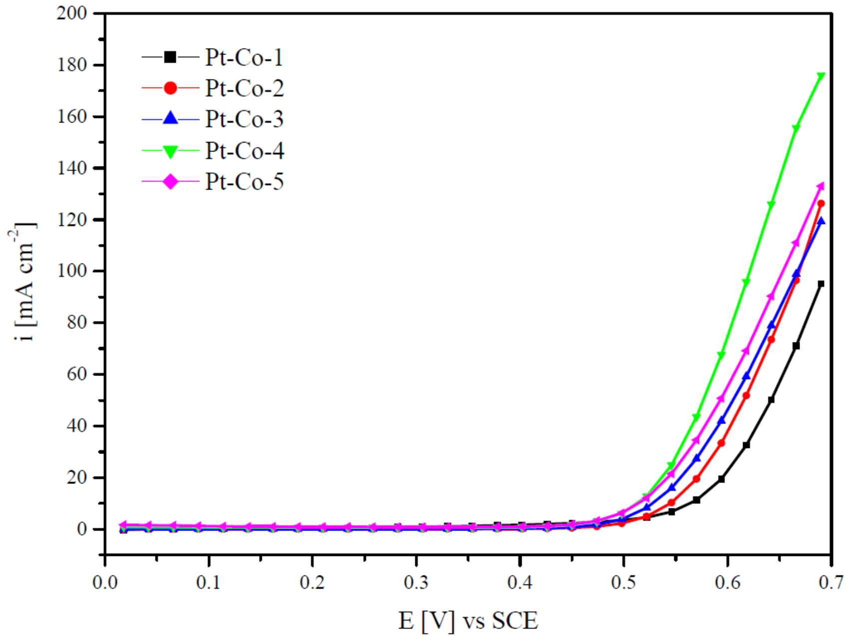

Figure 10. Linear voltammetry for OER in 1 M NaOH solution on selected Pt-Co electrodes

Pt-Co 1 shows a sluggish OER process with an onset potential around 0.55 V vs. SCE and a Tafel slope of 137 mV dec^{-1} in comparison to other samples. The Pt-Co-4 exhibits the lowest onset potential, developing the highest current densities. The kinetics of the OER, on the studied electrodes are characterized by a Tafel slope in the range of 137 mV dec^{-1} to 227 mV dec^{-1}. Similar studies conducted on Pt-Co supported electrodes in alkaline aqueous solutions [16] revealed a comparable behaviour. The activity of Pt-Co catalysts is significantly improved when increasing the Co concentration in the deposition electrolyte. The increased surface area, as well as the chemical composition ($CoPt_3$ alloy) are considered to contribute to an improved catalytic activity. Nevertheless, the enhancement of the OER can be ascribed to the presence of cobalt in the platinum structure, due to the structural changes caused by alloying (increase in d-band vacancy) and geometrical changes (decrease of the Pt-Pt bond distance) [17], providing more favorable sites for dissociative adsorption and desorption of oxygen. Similar studies have shown that by alloying platinum with metal elements which present smaller atomic size cause lattice contraction being more active, while the alloys with metals with larger atomic size lead to lattice expansion and are less active [18].

Table 5. Kinetic parameters for OER in 1 M NaOH solution

Sample	***b*** **[mV dec^{-1}]**	***α***	***i*$_0$** **[A m^{-2}]**
Pt-Co-1	137	0.43	8.74
Pt-Co-2	166	0.36	25.32
Pt-Co-3	209	0.28	54.55
Pt-Co-4	223	0.26	101.03
Pt-Co-5	227	0.26	76.81

The catalytic activity of the Pt-Co electrodes was investigated regarding the ORR in situ in a PEMFC test bench. MEA were produced as previously described for Pt/CNF electrodes testing. The polarization curves for Pt-Co electrodes employed as cathodes are presented in Figure 11. the OCV for the investigated samples is lower than 0.95 V. Likewise, the highest voltage drop occurs in the small current densities region (0 – 100 mA cm^{-2} mg^{-1} Pt) being correlated to the activation energy barrier. Sample C1 presents the higher activation polarization loss, which can be explained by the smaller platinum-cobalt loading in comparison to the other investigated samples. Polarisation curves display a maximum power density of 300 mW cm^{-2} mg^{-1} Pt associated with a current density of 500 mA cm^{-2} mg^{-1} Pt (at 500 mV) for sample C3. Cathodes C1 and C2 show lower values due to the smaller catalyst amount. Likewise, differences in the polarisation behaviour are assigned to deposition parameters of the Pt-Co alloy catalyst which determine the catalyst loading.

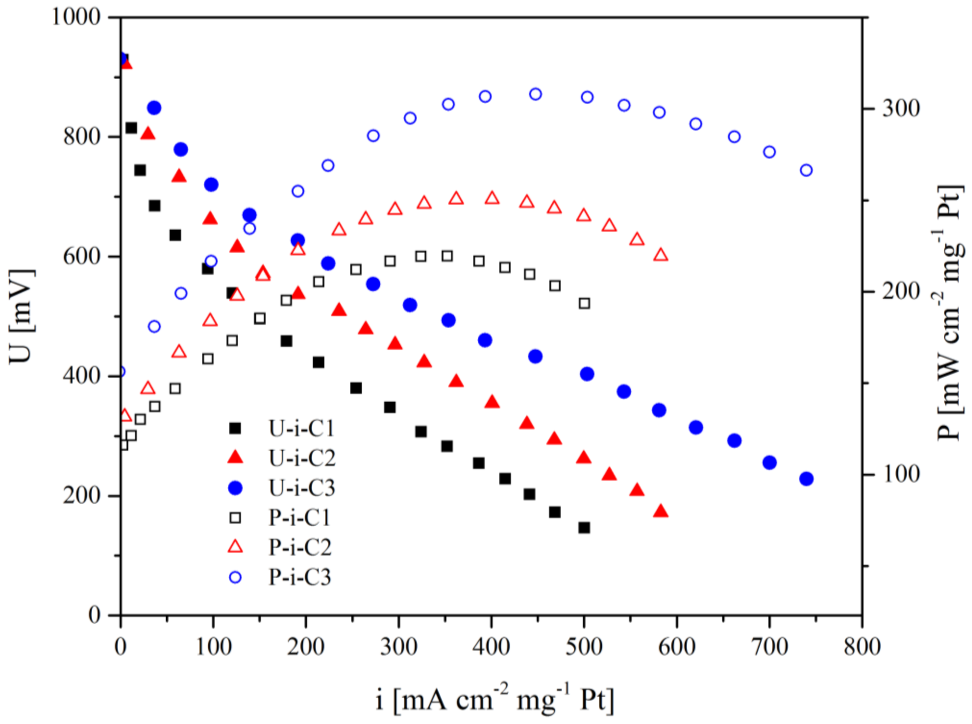

Figure 1. Polarization curves of MEA prepared with the same Pt/C anode and: C1 – Pt-Co/CNF 50 mA cm^{-2},5000 cycles, C2 – Pt-Co/CNF 100 mA cm^{-2}, 5000 cycles; C3 – Pt-Co/CNF 100 mA cm^{-2} 10000 cycles

3. Conclusions

The presented method leads to a facile and rapid way to develop electrodes with an improved catalytic activity promoted by the presence of platinum, the most electroactive metal and by the employment of a support material with high specific surface area. Moreover, alloying platinum with transitional metals like cobalt reduces significantly the production costs and improves substantially the durability of the catalysts.

The original research described in the present work consists in a theoretical study on available literature data regarding catalyst materials, fabrications methods and applications. The focus was directed to aspects concerning the production of novel catalyst materials suitable for PEMFC and water splitting electrolysers and regarding the development of effective methods to improve the catalytic activity, stability and durability of the discussed electrodes respectively.

The present work dealt with the development of catalyst materials based on carbon nanofibers using an **electrochemical method**. The CNF provide a high surface area for the catalyst particles, improving considerably the active surface area. The electrodeposition process has several advantages in comparison to other available methods, being more efficient at low operating costs, conferring also an easier control for the nucleation and growth of the metal particles and providing a higher utilisation degree of the catalyst particles. Moreover, this technique provides a simple fabrication way for the electrodes and guarantees that the ions from the plating bath, pass through the electrolyte towards the support material and are deposited on the areas where protonic and electronic conduction coexist. This condition is mandatory for developing fuel cell catalyst materials due to the essential demand of three-phase zones existence. In addition, this method proved to be an efficient way to synthesize catalyst nanoparticles with high density of atoms and clean surfaces, since this process does not require the addition of stabilizers which may be adsorbed onto the electrode surface, poisoning the active area of the catalyst. Furthermore, applying this method, the control of the microstructure and thickness or chemical composition in case of an alloy deposition is facilitated. The pulsed current deposition technique has also several advantages in comparison to direct current electrodeposition, as it can provide a better current distribution and controlled mass transfer step. Additionally, the deposition is more uniform and the porosity is reduced.

Furthermore, it is strongly necessary to correlate the deposition technique with an appropriate functionalization treatment to achieve improved catalysts materials with low platinum loading. In this regard, a chemical-physical process based on oxygen plasma was applied on the CNF support material, generating functional acidic groups directly onto their outer surface. **Plasma functionalization** produces covalent chemical bonds between oxygen and carbon atoms facilitating the further interactions between the treated material and other substances or environment due to their polarity. Such chemical bonds are stable over time and there is no degradation under normal storage conditions. This treatment is based on an efficient and rapid process, providing a high functionalization degree onto the exposed material. In addition, no by-products are released during the operation and the process can last a few minutes in comparison with other available functionalization methods.

The main topic of the present thesis is well correlated with the actual major problems encountered in the development catalyst materials with low platinum loading and moreover, this work aims to contribute to several research questions related to the state of the art in the field of PEMFC.

This study focused on the development of two types of catalyst materials suitable for electrochemical applications, based on carbon nanofibers decorated with **platinum**

nanoparticles and **platinum-cobalt alloy nanoparticles** respectively. As state of the art in the PEMFC indicates, the platinum based catalysts are produced for the anodic side of a fuel cell, where the hydrogen oxidation reaction takes place. On the other hand, the cathodic reaction is considered more complicated than the anodic one, because it can consist in two distinct routes and the major voltage losses in a PEMFC system are caused by the high oxygen reduction overpotential. Moreover, the catalyst material needs to be very resistant for the increased corrosive conditions that occur on the cathodic side of the fuel cell. Consequently, the cathode needs either a higher platinum loading than the anode or a suitable platinum alloy, to overcome the afore mentioned difficulties. In the actual state of the art it is mentioned that platinum alloyed with transitional metals significantly improves the catalytic activity for the cathodic reaction, reducing the dissolution and migrations phenomena of platinum particles and increasing the catalyst durability respectively. Concerning these aspects, a platinum – cobalt alloy catalyst was developed for the OER as well as for the cathodic side of the fuel cell. The obtained electrode materials were characterized using various techniques such as SEM, EDX, XRD, XRF, TGA, LV and CV. Moreover, the behaviour of the obtained electrodes as catalysts for PEMFC was investigated plotting in situ polarization curves.

Finding a bifunctional catalyst that is both stable and active for HER/OER and HOR/ORR respectively has represented a major research focus in the field of electrocatalysts. Although Pt is nearly ideal for HER, HOR and ORR, it has shown poor OER activity due to the reduced surface area and formation of a platinum oxide layer that behaves as an electrical insulator. These aspects may be overcome by using a catalyst consisting of conventional Pt and Co particles.

Using the described method, low platinum loading electrocatalysts have been synthetized. The activity of the electrodes is attributed to the higher electrochemical surface area achieved by applying platinum nanoparticles. Moreover, the support material played a significant role for increasing the active surface area, by providing a higher available surface. The high utilisation degree of the deposited platinum particles achieved by applying an electrochemical method had also a significant influence on the catalyst activity.

The obtained electrodes present a bifunctional character. Pt/CNF electrodes are suitable as catalyst materials either for HER in acidic environments, as well as for HOR inside a PEMFC. Likewise, Pt-Co/CNF catalysts have been proven to catalyse the OER in alkaline mediums and moreover, the catalytic behaviour as cathodes inside a PEMFC was also noticed.

4. References

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