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Development of Ni-based Electrocatalysts for Hydrogen Production in a PEM-type Hydrogen Generator

by

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A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the Degree of Master of Engineering

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A mis padres con todo el amor del mundo...

A mis abuelas...

A Emma...

ABSTRACT

Results on the development of Ni-based electrocatalysts for hydrogen evolution in an acidic medium are discussed in the thesis. This topic is of a great importance for the development of a PEM-type hydrogen generator, as a global initiative for the development of clean sustainable energy systems. A number of experimental techniques were used in research: linear *dc* polarization (Tafel), electrochemical impedance spectroscopy (EIS), potential-decay, inductively coupled plasma (ICP), X-ray diffraction (XRD), and scanning electron microscopy (SEM). The first part of the thesis discusses the results on the influence of alloying nickel by left-hand side transition metals (Fe, Mo, W) on the electrocatalytic activity in hydrogen evolution, while the second part of the thesis discusses the results on the development of Ni electrocatalysts using conductive polymers, polypyrrole (PPY) and polyaniline (PANI) as catalysts pattering matrices.

The results presented show that alloying nickel with left-hand side transition metals (Fe, Mo, W) results in an increased electrocatalytic activity in the HER when compared to pure nickel. Two effects were found to be responsible for the observed behavior: the increase in surface roughness and the increase in intrinsic activity of the material. All bimetallic coatings were found to offer higher overall electrocatalytic activity than pure nickel, and the prevailing factor that contributes to this was found to be the increased surface roughness. NiMo-1 (Ni_{7.3}Mo) was found to yield the highest overall electrocatalytic activity among the investigated materials. On the other side, NiW-1 (Ni_{3.4}W) was found to yield the highest intrinsic electrocatalytic activity, which was postulated to be due to the modification of the electron density in the *d*-shell upon alloying nickel with tungsten. It was noticed that the increase in crystallinity can contribute to the increased electrocatalytic activity in the HER.

It was shown that pattering a glassy carbon electrode surface with conducting polymers (CP) offers a convenient method of increasing a surface area of the nickel electrocatalytic coating. The influence of a CP matrix thickness and Ni loading on the overall HER electrocatalytic activity was investigated. It was demonstrated that Ni / CP electrocatalysts offer significantly higher HER electrocatalytic activity when compared to a classical nickel layer electrodeposited on a copper substrate. This was explained on the basis of the increased surface roughness (area) of the Ni / CP coatings. It was also shown that the morphology of the electrodeposited CP matrix greatly influences the overall electrocatalytic activity of the Ni catalyst layer.

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RÉSUMÉ

Les résultats sur le développement d'électrocatalyseurs à base de nickel (Ni) pour la production électrolytique d'hyrogène dans un milieu acide sont discutés dans cette thèse. Ce sujet est d'une grande importance pour le développement d'un générateur d'hydrogène de type PEM (membrane échangeuse de protons), comme initiative globale pour le développement de systèmes d'énergie durables et propres. Plusieurs techniques expérimentales ont été utilisées durant cette recherche : la polarisation linéaire de courant directe (Tafel), la spectroscopie d'impédance électrochimique (EIS), le potentiel d'appauvrissement, le plasma inductif couplé (ICP), la diffraction par rayon-X (XRD), et la microscopie électronique à balayage (SEM). La première partie de la thèse discute des résultats de l'influence d'allier le Ni avec les métaux de transition (Fe, Mo, W) sur l'activité électrocatalytique de la production d'hydrogène, et la deuxième partie de la thèse discute des résultats sur le développement de l'utilisation d'électrocatalyseurs à base de Ni avec des polymères conducteurs (CP) tels que le polypyrrole (PPY) et la polyaniline (PANI) comme matrices catalytiques.

Les résultats présentés démontrent qu'allier le Ni avec les métaux de transition (Fe, Mo, W) permettent une amélioration de l'activité électrocatalytique de la production d'hydrogène (HER) par rapport à celle du Ni pur. Ceci est dû à l'augmentation de la rugosité de surface et de l'activité électrocatalytique intrinsèque du matériau. Il a aussi été démontré que tous les revêtements bimétalliques ont une plus grande activité électrolytique que le Ni pur, ce qui est principalement dû à l'augmentation de la rugosité de la surface. Les résultats prouvent que le NiMo-1 (Ni_{7,3}Mo) présente la plus grande activité électrocatalytique intrinsèque, à cause de la modification de la densité électronique de la couche électronique-*d* lors de l'alliage du Ni avec le W. Il a été constaté que l'augmentation de la cristallinité contribue à l'amélioration de l'activité électrocatalytique de la production d'hydrogène.

Il a été démontré que le dépôt de polymères conducteurs (CP) contenant des particules de Ni, à la surface d'une électrode de carbone vitreux, est une procédure adéquate car elle permet d'augmenter la surface active de la couche de Ni. L'influence de l'épaisseur de la matrice des polymères conducteurs (CP) et du chargement en Ni sur l'activité électrolytique de la production d'hydrogène ont été étudiées. Ces expériences

ont montré que les électrocatalyseurs de Ni / CP offrent une activité électrolytique significativement plus grande pour la production d'hydrogène comparativement à une simple couche de Ni électrodéposée sur du cuivre. Ceci est dû à l'augmentation de la rugosité de la surface des revêtements de Ni / CP. Les résultats indiquent aussi que la morphologie de la matrice de polymères conducteurs électrodéposées influence grandement l'activité électrolytique de la couche de catalyseur de Ni.

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CHAPTER 1

1. INTRODUCTION

Several converging forces explain the renewed interest in hydrogen. Technological advances and the advent of greater competition in the energy industry are part of the equation. But equally important motivations for exploring the different uses of hydrogen are the energy-related problems of energy security, air pollution, and climate change – problems that collectively call into question the fundamental sustainability of the current energy system [1].

Hydrogen, the simplest element and most abundant element on earth, is one of the most promising energy carriers for the future. It is a high efficiency, environmentally friendly fuel that can be produced safely. It is versatile, and has many potential energy uses, including powering homes, a variety of industrial activities, electric utilities and non-polluting vehicles. Moreover, hydrogen is anticipated to join electricity as the foundation for a globally sustainable energy system using renewable energy (solar, wind, hydro) making it the cleanest and simplest sustainable ideal fuel. Therefore, hydrogen is increasingly considered as *the fuel of the future* [1-4].

The most common and least expensive way to produce hydrogen at present is by steam methane reforming. The U.S. Department of Energy (DOE) reports that roughly 48% of the worldwide hydrogen production comes from this fully commercial process. However, this technology also generates carbon monoxide (which is dangerous to health and represents the major poison for hydrogen fuel-cell catalysts, and also for catalyst used in various industrial processes occurring at low temperatures, <150°C), and carbon dioxide (the primary greenhouse gas). Although there are several other methods to produce hydrogen, the most promising long-term technique is water electrolysis, where electricity is used to split water into hydrogen and oxygen. It represents *the only* process where hydrogen can be produced by true renewable and fully environmentally friendly energy sources. Currently, electrolysis provides only a small percentage of the world's hydrogen (only 4% reported by U.S. DOE), most of which is supplied to applications requiring small volumes of high purity hydrogen (or oxygen).

Currently, the water electrolysis process is carried out under alkaline conditions. However, there are many disadvantages to this process, which will be stated in the following section. Alternatively, the use of solid polymer electrolyte membrane (PEM)– type generators based on the fuel-cell technology to produce hydrogen from demineralized water would offer a number of advantages compared to the classical alkaline process, especially for residential and small-scale applications. One of the main obstacles associated with the large-scale commercial application of the PEM hydrogen generator, however, is related to high investment costs, mainly due to the use of noble metals (Pt, Ir, Ru) as electroactive catalyst materials to produce hydrogen. Therefore, there is a major need to develop new electrocatalitic materials.

The aim of this research project is related to the improvement of electrolytic production of hydrogen utilizing new active, efficient, stable, and low cost electrocatalysts for water splitting in the PEM hydrogen generator. This thesis also represents the first report on the use of conducting polymers to pattern the electrode surface based on nickel as a catalyst material.

The thesis is divided into six chapters. Chapters 1 and 2 present an introduction to the subject and the theoretical background, respectively. In these sections the PEM technology is described as well as the characteristics of the hydrogen evolution reaction (HER) and the electrocatalyst development. Chapter 3 states the objectives of this study. Chapter 4 describes the experimental procedures and techniques employed. Chapter 5 presents all the experimental results and the discussion. Finally, chapter 6 contains the conclusions and suggestions for future work. Part of the numerical data generated is tabulated in the appendices.

CHAPTER 2

2. LITERATURE REVIEW

2.1 Technology of water electrolysis

The history of water electrolysis starts as early as the first industrial revolution, when, in the year 1800, Nicholson and Carlisle discovered the ability of water splitting. By 1902 more than 400 industrial water electrolyzers were in operation, and in 1939 the first large water electrolysis plant with a capacity of 10,000 m³ H₂ h⁻¹ went into operation, and in 1949 the first pressurized industrial electrolyzer by Zdansky/Lonza was built [5]. However, the history continues to our days with the development of a new technology (PEM-type generators), and the optimization and reconstruction of the old technology (alkaline water electrolyzers).

2.1.1 Alkaline Technology

Despite the fact that the discovery of electrolytical water splitting was made in acidic water -in industrial plants the alkaline medium is preferred- because corrosion is more easily controlled and cheaper construction materials can be used than in acidic electrolysis technology [5].

The electrolyte used in conventional alkaline water electrolyzers has traditionally been aqueous potassium hydroxide (KOH), mostly with solutions of 20-30 wt% because of the optimal ionic conductivity and remarkable corrosion resistance of stainless steel in this concentration range. The typical operating temperatures and pressures of these electrolyzers are 70-100°C and 1-30 bar, respectably [6].

Physically an electrolyzer stack consists of several cells linked in series. Two distinct cell designs exist: monopolar and bipolar. In the monopolar design (Figure 2.1a) the electrodes are either negative or positive with parallel electrolytical connection of the individual cells, while in the bipolar design the individual cells are linked in series electrically and geometrically [6]. In both designs a membrane is placed between the cathode and de anode, which separate the hydrogen and oxygen as the gases are produced, but allows the transfer of ions [7].

3



(b)

Figure 2.1 Principle of (a) a monopolar and (b) bipolar electrolyzer [6].

The bipolar electrolyzer (Figure 2.1b) is of a slightly more complicated construction that involves filter-press and allows for high-pressure/high-temperature production, making it more efficient and compact [8]. However, the manufacturing costs

are higher compared with the simple and sturdy monopolar electrolyzers. Nevertheless, most commercial electrolyzers manufactured today are bipolar [6].

In an alkaline system the reactions at each electrode are [6]:

Cathode:
$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$
 (2.1)

Anode:
$$2OH^- \rightarrow \frac{1}{2}O_2 + 2H_2O + 2e^-$$
 (2.2)

The principle of alkaline water electrolysis is shown schematically in Figure 2.2 [6].



Figure 2.2 Operation principle of alkaline water electrolysis [6].

Although the electrolysis process is ordinarily carried out under alkaline conditions, there are many disadvantages to the alkaline process such as: high energy consumption, low specific production, low efficiency (between 60 and 80%) and voluminous systems, and safety issues related to use of caustic electrolytes. Other important fact is this technology is not suitable for residential or small scale applications due to the toxic caustic electrolyte and the voluminous systems.

Some implementations can improve the design of advanced alkaline electrolyzers used in industry, such as: (1) new cell configurations to reduce the surface-specific cell resistance despite increased current densities (e.g. zero-gap cells and low resistance diaphragms), (2) higher process temperatures (up to 160°C) to reduce electric cell resistance in order to increase the electric conductivity of the electrolyte and improve the kinetics of hydrogen and oxygen evolution, and (3) new electrocatalysts to reduce anodic and cathodic overpotentials [6]. However, the use of solid polymer electrolyte membrane (PEM)–type generators, with demineralized water as the raw material, would offer a viable alternative to the alkaline process, especially for residential and small scale applications.

2.1.2 PEM hydrogen generators

Solid polymer electrolyte (SPE) water electrolysis technology, now called proton (or polymer)-exchange membrane (PEM) technology, has been subject of many researches since General Electric Company's pioneering work in the late 1960s. More recently the Swiss firm ABB developed its MEMBREL process for both water electrolysis and ozone generation. Japan is also active in this field with the work performed under the Sunshine project [9]. Basically, this technology consists of coating or hot pressing two electrocatalyst layers on to a PEM membrane used as electrolyte.

2.1.2.1 Membrane materials

Present day PEM materials are perfluorosulphonic-acid polymers -i.e. plastics having many of the physical attributes of Teflon. These materials are long chain polymers, consisting of CF_2 backbones with SO_3 -terminated CF_2 side groups [10]. Charge carriers in the membrane are hydrated hydrogen ions which move through the solid electrolyte by passing from one sulphonic acid group to the next one ('hopping' mechanism). The acid groups in the membrane create a highly acidic environment (equal to that of a 20 wt% sulfuric acid solution); therefore, acid resistance metals must be used for electrocatalysis [11].

Du Pnont's Nafion[®] products are generally chosen as solid electrolyte because of their intrinsic properties: excellent chemical and mechanical stability, high ionic

conductivity and gas permeability. However, Dow Chemical has also developed membranes with very similar characteristics [11].

2.1.2.2 Cell configuration

On the two faces of the membrane the anode (usually Ir or IrO_2) and the cathode (platinum) metals are bonded (chemically or by hot press technique) using different procedures. This configuration is called a *membrane electrode assembly* (MEA), which is also used in the fuel cell technology. A stable conductive material used as a separator between the anode chamber of one cell and the cathode chamber of the adjacent cell also serves as a current collector in a bipolar configuration. Water decomposes electrochemically in the anode chamber producing O_2 gas, hydrogen ions and electrons. The hydrogen ions move through the PEM membrane and recombine electrochemically with electrons at the surface of a cathode catalyst to form hydrogen gas in the cathode chamber as shown in Figure 2.3 [12].



Figure 2.3 Schematic representation of two PEM single cells connected in a series [12].

In a PEM system the reactions at each electrode are:

Cathode:
$$2H^+ + 2e^- \rightarrow H_2$$
 (2.3)

Anode:
$$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$$
 (2.4)

In order to achieve highly efficient electrolysis, the ideal PEM must have the following characteristics: (1) Catalyst film deposition predominantly within the Nafion thin (sub micron) layer adjacent to the membrane surface; (2) large electrode –membrane contact area to provide electrochemically large active surface area; (3) good inter particle contact for low electronic resistance; and (4) porous structure for free mass transfer of water and gases, a large 3D reaction zone that enhances a two-interface contact (hydrogen ion/electrocatalyst and electron/electrocatalyst) [12].

2.1.2.3 Advantages and disadvantages of PEM hydrogen generators

The use of solid polymer electrolyte membrane (PEM)-type generators based on the fuel-cell technology to produce hydrogen from demineralized water, would offer a number of advantages compared to the classical alkaline process: this technology is safer and more reliable since no caustic electrolyte is circulated in the cell stack; it operates at higher currents and efficiencies. It is a small volume system, it produces higher gas purity, and offers the construction simplicity and lower maintenance costs. In addition some membrane materials could sustain high differential pressure without damage and are efficient in preventing gas mixing [9]. Another important aspect is that the fixed nature of the electrolyte allows a quick start up, and more significantly, a rapid shut down because there is no need to circulate the electrolyte until the reagents are removed in order to prevent explosive mixing [10].

For all the reasons cited above this technology is promising especially for residential and small-scale applications. However, one of the major obstacles associated with the large-scale commercial implementation of this technology are the high investment costs mainly due to the use of noble metals (Pt, Ir, Ru, Rh) as electroactive catalyst materials. There are several groups in the world that are working on the development of PEM-hydrogen generators, but to the best of our knowledge, the

corresponding technology is based only on the use of noble metals as electrocatalysts. Also, some other advantages offered by the fuel-cell technology (i.e. the use of Vulcancarbon supported electrocatalysts layers for the MEA) have not yet been investigated. Therefore, there is a major need for development of new active, efficient, stable, and cheap (non-noble) electrocatalysts for water splitting in the PEM hydrogen generator, which would offer low overpotentials for the hydrogen evolution reaction at high current densities (1 - 2 A cm⁻²). Also, there is a great need to construct better MEAs, which would be based on the nano-technology used for the construction of low-temperature fuel-cell MEAs.

With the development of an affordable PEM hydrogen electrlyzer, the transition to a new world based on clean sustainable energy would be possible. That is why the aim of this project is to find new candidate materials with equal or better characteristics than the materials presently used to produce hydrogen in a (PEM)-type generator.

2.2 HER Electrocatalysis

Research in the area of HER catalyst development has been mainly focused on several areas of interest: (*i*) intrinsic nature of the reaction [13-16], (*ii*) electrode composition [17-21], (*iii*) surface morphology [13-15,21-26], (*iv*) structural, chemical and electronic properties [17-20,27,28], and (*v*) physical, chemical and electrochemical activation treatments[13-15,29-31].

In the electrolysis of water for a hydrogen production system, the cathodic electrode is required to have low hydrogen overpotential in view of the least energy consumption [32]. The desired decrease in overpotential can be achieved by choosing a highly catalytically active electrode material for the HER and/or by increasing the active surface area of the electrode. In respect to the former, several attempts have been made to explain the characteristics of hydrogen overpotential of individual metals using various physical and/or electronic parameters, including the atomic number [33], the work function [34], the bond-strength of metals [35], the heat of adsorption of hydrogen on metals [36], and the electronegativity [37]. Overall, it has been concluded that the intrinsic catalytic activity for the HER can be related to the electronic structure of metals, although any explicit and comprehensive explanation has not yet been given.

Unfortunately, it is clear that, except precious metals, other less-noble pure metals express much lower activity towards the HER [36]. However, the commercial use of noble metals as a cathode for water electrolysis is very limited because of its high cost. Instead, much attention has been paid to transition metal-based binary alloys. Certainly, the combination of two transition elements could result in enhanced electrocatalytic activity, which could be close or possibly higher than that of individual noble metals. Such an alloying effect it is known as the electrocatalytic synergetic effect. The theoretical approach to explain the HER activity of alloy catalysts, however, is even more complex than for pure metals, and several theories have been proposed. The alloying effect of transition metal-based alloys on both hydrogen evolution activity and catalyst stability has been discussed on the basis of the Engel-Brewer valence-bond theory [27,28], and on the basis of the electronic structures of alloys; in particular, the direction of electron transfer between constituting atoms in the alloy and its effect on the respective Fermi levels of the components [18-20,27,28]. The well-known 'spillover' process in heterogeneous catalysis has also been used to interpret the synergism of transition metal based HER alloys [17].

In respect to the enhancement of the electrocatalytic activity by increasing the active surface area of the electrode, Ni-based Raney-type alloys have been successfully used to fabricate HER cathodes in classical types of alkaline electrolyzers [14,15,26,30]. However, these types of electrodes would not be suitable for the PEM-type hydrogen generator, due to a very limited contact area between the solid electrolyte membrane and the active catalyst layer. Hence, direct plating of Pt, Ru and Ir onto the polymer membrane has been used as a catalyst preparation method [38,9] -i.e. fabrication of the membrane electrode assembly (MEA). However, beside very high costs associated with the use of these noble metals, one of the main drawbacks of the presently used MEA preparation methods is a relatively low catalyst efficiency-to-loading ratio, which is mainly due to the limited polymer electrolyte/catalyst interface area -i.e. the threedimensional (3D) reaction zone. A possible solution to the problem is a construction of the MEA similar to the construction used in the PEM fuel cell [39], which would allow for lower catalyst loading to be used. Nevertheless, since the state-of-the-art catalyst in the PEM fuel cell technology is still Pt or Pt-Ru (depending on the fuel type used), there still remains an issue of a cheaper catalyst material to be designed for the use in the PEMtype hydrogen generator. However, based on the literature overview on the HER

electrocatalysis in the aqueous media, nickel would offer the best (and cheapest) starting point for the development of PEM hydrogen catalysts.

During the few past decades, many papers have illustrated the development of new electrode materials for HER using transition metal-based alloys, especially Ni based alloys (a thorough literature outline of the HER electrocatalysis was already presented previously in the text). Indeed, Ni and nickel alloys exhibit good catalytic activity for the HER and high corrosion stability. Most often electrodeposition from suitable baths is employed to produce the electrodes. Sometimes electrodes are metallurgically prepared by arc melting of the pure components under argon atmosphere, for example [40,18,19,41]. Numerous studies have thoroughly investigated the kinetics and mechanism of Ni-based alloys, like Ni-Mo, Ni-W or Ni-Fe in alkaline media, but surprisingly Ni-based alloys in acidic media have not been widely studied (which is mostly due to the fact that the research focus in this area has been on classical alkaline electrolyzers). However, since a PEM generator works at very low pH values, studies done at high pH's cannot offer quite reliable data for the design of PEM-catalyst. Hence, a thorough investigation of possible catalyst materials in an acidic environment is required in order to support the development of the PEM hydrogen generator technology. Therefore, this thesis represents an attempt to contribute to the development of active, efficient, stable, and cheaper nickel based electrocatalysts for hydrogen production by water electrolysis in the PEM hydrogen generator. The aim of the project was not to develop 'industry-ready' catalytic surfaces, but rather to investigate and point-out to fundamental factors that could contribute to the development of better HER catalysts in the acidic media (*i.e.* PEM media).

2.3 Electrocatalysis at conducting polymer electrodes modified with dispersed metals

The aim of the second part of the project was to study the feasibility of using conductive polymers (CP) -i.e. polypyrrole and polyaniline-, for its possible application as catalyst substrates (matrices) for a PEM hydrogen generator. A great deal of attention has been paid to the use of conducting polymers as supporting matrices for the immobilization of catalytically active metal particles [42]. Indeed, porous structure and high surface area of many conducting polymers (like polypyrrole, polyaniline and

polythiophene) favour their use as supporting material for the development of new catalytic and electrocatalytic materials. The dispersion of metal particles into a polymer matrix provides the possibility of high specific areas of metal catalysts and, thus, improved catalytic efficiency. This would be a good approach to improve the contact area between the solid electrolyte membrane and the active catalyst layer in the PEM hydrogen generator.

Apart from noble metals, some different metals have been rarely dispersed in conducting polymers and used in electrochemical processes. Casella et al. [43] dispersed copper microparticles in PANI film by electroreduction and used it for electroanalytical detection of amino acids and polyhydroxylic alcohols in alkaline media. Abrantes et al. [44] studied electrocatalytic activities of modified electrodes, which were prepared by electroless incorporation of Ni-P particles in poly(3-methylthiophene) films. Bouzek et al. [45] have dispersed platinum in a polypyrrole film in order to modify an anode for the hydrogen fuel cell. Leger and Lamy's group have done extensive studies on the use of Pt-based catalyst dispersed in a conducting polymer layer as anodes for oxidation of small 'C1' molecules (methanol, formaldehyde and formic acid) that are interested for the fuel cell applications [43]. However, in all these studies the conducting polymer matrix was used as an anode matrix, since polypyrrole and polyaniline are conductive in the anodic region. On the other side, under the cathodic polarization, they become insulators and can serve only as a matrix material in which an active catalyst is dispersed. However, one must then ensure the electric contact between the dispersed catalyst and the electron-conducting substrate.

2.4 Electrochemically synthesized PPY and PANI coatings

Among organic materials, conductive polymers (or conjugated polymers CPs) have attracted most attention for possible in many fields because of their unique properties and versatility. The main characteristic of these polymers is their conjugated π system, which extends beyond the monomer and allows and electron delocalization along the polymer chain, and gives a conductive character to the material [46]. The conductivity of these polymers can be tuned from insulating regime to superconducting regime, by chemical modification (i.e. by the degree and nature of doping) [47]. Conjugated polymers can be prepared by both electrochemical and chemical methods. The chemical synthesis can be performed by oxidation or reduction of the monomer, in

liquid or gas phase, sometimes by thermal autopolymerization [46]. The polymers obtained by chemical synthesis are expected to have ordered structures [47]. Electrochemical methods have advantages over chemical methods in the sense that they offer control on the polymerization and doping level, and could be produced over a number of substrates in order to fabricate devices directly [47]. By using electrochemical methods, these polymers can be synthesized by anodic oxidation of the monomers in suitable electrolytes (aqueous or non- aqueous) either at constant potential, or at constant current, or by cycling between different potentials [47]. Polymers obtained this way are in an oxidized state because the oxidation potential of the monomer is generally higher than that of the formed polymer [46]. The polymers are doped because the electroneutrality of the material is assured by the presence of counter-ions (anions) compensating for the positive charge carried by the skeleton in the oxidized state [46].

Although there are many conductive polymers with similar characteristics, this research is focused on the study of electroeynthesized polyaniline (PANI) and polypyrrole (PPY) as catalyst substrates for their possible use in a PEM hydrogen generator. The reason for this is that the two polymers are stable in an acidic environment (the PEM generator environment), are widely available, cheap, and easily synthesised. Another reason of using PANI and PPY is due to their quite different morphology (Figure 5.8), which was used as parameter in the design of HER catalyts. The molecular structures of both polymers are presented in Figure 2.4 and the polymerisation mechanism is shown in Figure 2.5.



Figure 2.4 Molecular structures of (a) polyaniline and (b) polypyrrole.



(b)



Figure 2.5 Polymerisation mechanisms of (a) polyaniline and (b) polypyrrole.

2.5 Hydrogen evolution reaction

During water electrolysis, the reaction that takes place to produce hydrogen gas at the cathode is called "hydrogen evolution reaction" (HER). This reaction is of great importance in fundamental and, nowadays, in technological electrochemistry as explained before. Consequently, many studies [13,29] have been conducted to understand the principles of the HER kinetics and mechanisms.

It is well established that the HER on a metallic electrode M, in acidic media, proceeds according to the following three-reaction mechanism [48]:

$$M + H^{+} + e^{-} \leftrightarrow M - H_{ads}$$
 (2.5)

$$M-H_{ads} + H^{+} + e^{-} \leftrightarrow H_{2} + M$$
(2.6)

 $M-H_{ads} + M-H_{ads} \leftrightarrow H_2 + 2M$ (2.7)

The first reaction is an electroreduction of a proton with a formation of hydrogen adsorbed on the electrode surface (Volmer reaction (2.5)), followed by electrochemical desorption of hydrogen (Heyrovsky reaction (2.6)) and/or chemical desorption of hydrogen (Tafel reaction (2.7)). M represents the free metal (electrocatalyst) surface and M-H_{ads} the atomic hydrogen adsorbed on the metal surface. The adsorbed hydrogen atom plays a key role in the mechanism and kinetics of the hydrogen evolution reaction, changing both its thermodynamics and kinetics. The both mechanisms require the formation and then cleavage of M-H_{ads} bond. Hence, the reaction rate for the HER is determined by the strength of proton adsorption bonding to the metal surface. The maximum rate of hydrogen evolution will occur at intermediate values of M-H_{ads} bond strengths, resulting in a behavior characterized by the well known 'volcano curve' [36]. This volcano curve is made for pure metals, and there is, definitely, a trend in the HER reaction rate and the position of the metal in the periodic table. Since hydrogen is an electron donor, left-hand side transition metals with semi-empty d-orbitals (e.g. Ti, Zr, V, Ta, etc.) make a stronger M-H_{ads} bond, while the right-hand side transition metals with full d-orbitals (e.g. Cu, Zn, Au, Hg, etc.) make a weak M-H_{ads} bond. Consequently, neither of them will be a good HER catalyst. On the other side, Pt- and Ir-group of metals have almost filled d-orbitals, thus making the M-H_{ads} bond of an intermediate strength.

This is, actually, the basis for the design of cheap non-noble HER catalyst, since by combining e.g. Ni with some of the transition metals (from the left side of the series) results in the change of the electron density of states in the outer d- shell, thus changing the strength of the M-H_{ads} bond. This is the basis of the first part of the project described in this thesis. It will be shown that the electron density change, resulting from the combination of Ni and other transition metals (Mo, W, Fe), significantly influences the HER kinetics. However, some other factors (surface diffusion, morphology, grain-size and grain-dislocations) also play a role in the HER kinetics, but there is no a common agreement in the literature about these factor, but rather few isolated studies.

CHAPTER 3

3. OBJECTIVES

The present work is part of a more general program, currently in progress in this laboratory, to identify and develop new candidate catalyst materials based on nanostructured hypo-hyper-d-electronic combinations of transition metals, which would exhibit enhanced synergism in the HER and possibly exceed electrocatalytical activity of individual noble metals.

The main specific objectives of this project are outlined as follows:

- To synthesize new catalyst materials for the HER that are based on nanostructured hypo-hyper-d-electronic combinations of transition metals, namely Ni-M (M = Ni, Mo, W, and Fe).
- To investigate the catalysts' structural composition, surface morphology and constituents surface distribution.
- To investigate the catalysts' overall and intrinsic catalytic activity in the HER.
- To investigate a possibility of using conductive polymers (polypyrrole and polyaniline) as catalyst pattering matrices for the development of Ni HER catalyst, with the aim to increase the catalyst active area.

CHAPTER 4

4. METHODOLOGY AND EXPERIMENTAL TECHNIQUES

4.1 Chemicals

All chemicals used in research were purchased from Sigma-Aldrich Company, and were used without further purification. All solutions were prepared using nanopure water of resistivity 18 M Ω cm. All experiments were performed at 22°C, unless otherwise specified.

4.2 Pretreatment of the electrode substrate

Electrode substrates used for the deposition of active electrocatalyst coatings went through careful pretreatment before the electrocatalyst coating was deposited. Two types of electrode substrates were used in the investigation: copper (Cu) and glassy carbon (GC). The experiments related to the synthesis of new Ni-based catalyst materials were done using a Cu electrode substrate, while the experiments performed with conducting polymers were made using a glassy carbon (GC) electrode substrate. The Cu substrate was chosen due to its excellent properties related to the adherence of metal coatings made by electrodeposition. Although Cu expresses some catalytic properties in the HER, the electrodeposited active coatings were compact and thick, thus insulating the Cu substrate from the electrolyte. On the other hand, since the conducting polymers are porous, the electrode substrate has to be inactive towards the HER. The GC substrate meets this condition entirely.

The pretreatment procedure involved the careful substrate surface cleaning by mechanical wet-polishing on a flat glass polishing pad employing #600 and #1500 grit sand paper. Then, the electrode substrates were thoroughly rinsed with distilled water, followed by cleaning in an ultrasonic bath for 6 to 7 minutes in order to remove polishing residues. Subsequently, the substrates were degreased with ethanol and rinsed copiously with nanopure water. This procedure was applied for both copper and GC substrates. However, the preparation of the GC substrate also included an electrochemical activation done by electrochemical cyclic polarization (40 cycles) in 0.5

M sulfuric acid between -1.5 and +1.0 V (vs. a mercury sulfate reference electrode - Hg/Hg_2SO_4) at a scan rate of 0.5 V s⁻¹.

4.3 Catalyst electrodeposition

The Cu substrate (94 mm in diameter) was used for the development of Ni-M (M = Ni, Mo, Fe, W) electrocatalysts, while the GC substrate (0.48 cm long and 0.36 cm wide) was used for the development of Ni / conducting polymer catalysts. The conducting polymers used were polypyrrole (PPY) and polyaniline (PANI).

4.3.1 Ni-M / Cu catalysts

The formation of Ni-M (M = Ni, Mo, Fe, W) coatings on the Cu substrate was done by the electrodeposition from their respective salt baths. The bath composition and deposition conditions are listed in Table 4.1[41,49-51].

Ni			NiW-1		
Current density	1600	A m ⁻²	Current density	100	A m ⁻²
Duration	20	min	Duration	30	min
Volume prepared	0.1	L	Volume prepared	0.1	L
pН	3.4		pH	10.5	
NiSO₄ • 6H₂O	300	g L ⁻¹	NiSO₄ • 6H₂O	80	g L ⁻¹
NiCl ₃ • 6H ₂ O	50	g L ⁻¹	Potassium citrate	50	g L ⁻¹
H₃BO₃	40	g L ⁻¹	Na ₂ CO ₃	excess	
Sodium lauryl sulfate	1	gL^{-1}	Na₂WO₄ • 2H₂O	20	g L ⁻¹
-		-			-
NiMo-1			NiFe-1		
Current density	1600	A m ⁻²	Current density	130	A m ⁻²
Duration	20	min	Duration	15	min
Volume prepared	0.1	L	Volume prepared	0.1	L
pН	10.5		рН	3.5	
NiSO₄ • 6H₂O	79	g L ⁻¹	NiSO ₄ • 6H ₂ O	80	g L ⁻¹
Na₂MoO₄ • 2H₂O	48	g L ⁻¹	FeSO₄ • 7H₂O	20	g L ⁻¹
Sodium citrate	88	gL^{-1}	sodium citrate	50	g L ⁻¹
NH₄OH	excess		Na ₂ CO ₃	20	gL^{-1}
			H₂SO₄	Until pH 3.5	_
			-		

Table 4.1 Experimental conditions used in electrodeposition of electrocatalytic coatings on a Cu substrate.

NiMo-2			NiFe-2		
Current density	1600	A m ⁻²	Current density	130	$A m^{-2}$
Duration	20	min	Duration	15	min
Volume prepared	0.1	L	Volume prepared	0.1	L
pH	10.5		рН	3	
NiSO ₄ • 6H ₂ O	52	g L ⁻¹	NiSO₄ ∙ 6H₂O	26	g L ⁻¹
$Na_2MoO_4 \cdot 2H_2O$	73	g L ⁻¹	FeSO₄ • 7H₂O	28	g L ⁻¹
Sodium citrate	88	g L ⁻¹	H₃BO₃	12	g L ⁻¹
NH₄OH	excess		Na₂SO₄	3.6	g L ⁻¹
			H₂SO₄	until pH 3	

Table 4.1 cont.

4.3.2 Ni/CP/GC catalysts

The formation of active Ni catalyst was done by (i) the electrodeposition of Ni on a preformed conducting/GC electrode substrate from the corresponding Ni-salt, and (ii) by the co-electrodeposition of Ni and conducting polymer on a GC substrate.

4.3.2.1 Deposition of Ni on a preformed conducting polymer substrate

The conducting polymer substrate was formed on a GC electrode substrate by the electropolymerization from the corresponding monomer solution. Electropolymerization was carried out at constant potential. The specific conditions and bath compositions are outlined in Table 4.2. The effect of different polymer deposition times was also studied.

Table 4.2 Experimental conditions used in electropolymerization of PPY and PANI	
coatings on a GC substrate.	

Conductive polymer	Plymerization soultion		Deposition Potential <i>vs</i> SCE (V)	Deposition times (min)	Notes
Polypyrrole	Pyrrole H₂SO₄	0.05 M 0.5 M	0.8	2.5 and 5	solution prepared two days before experiments
Polyaniline	Aniline H₂SO₄	0.05 M 0.5 M	0.82	2.5 and 5	solution prepared fresh before experiments

After the deposition of PANI or PPy, nickel was deposited electrochemically on the polymer film from its salt bath. The effect of electrodeposition time was also studied. The nickel bath composition and the deposition conditions are presented in Table 4.3.
Bath	n composition		Deposition Potential <i>vs</i> SCE (V)	Deposition times	Volume prepared (L)
NiSO ₄ • 6H ₂	O 26.2	g L ⁻¹		20 min and	
H₃BO₃ H₂SO₄	6.2 1.0	g L⁻¹ mM	-1.45	1 h 40 min	0.1

Fable 4.3 Experimental of	conditions used	in electrode	position of Ni	on a CP/GC substrate.
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4.3.2.2 Co-deposition of Ni and PPY on a GC substrate

In order to investigate if the electroactive surface area can be increased by changing the conducting substrate and active coating deposition conditions, a possibility of simultaneous formation of a Ni and PPY phase (co-deposition) was investigated. The co-deposition process was performed by cyclic voltametry at a scan rate of 0.1 V s^{-1} . The specific conditions were the following: the electrode was cycled between the deposition potentials of PPY and Ni, +0.8 and -1.45 V (vs. SCE) respectively, for a certain number of cycles; deposition starts at the PPY deposition potential and the experimental procedure is designed to wait 5 seconds after the first vertex potential and 2 seconds after the second vertex potential, meaning that PPY is electrodeposited for 5 seconds and then Ni is deposited for 2 seconds subsequently until the indicated number of cycles is completed.

The influence of the number of cycles on the electrocatalytic response was studied. The composition of the electrolytic codeposition bath and the number of cycles are presented in Table 4.4.

Bath con	nposition		Potential limits in cyclic voltammetry vs SCE (V)	Number of cycles	Volume prepared (L)	Notes
NiSO₄ • 6H₂O	26.2	g/L		20		prepared
H ₃ BO ₃	6.2	g/L	+0.8 and -1.45	and	0.1	two days
H₂SO₄	1.0	mМ		40	•••	before
Pyrrole	50.0	M				experiment

Table 4.4 Experimental conditions used in the co-deposition of PPY and Ni particles on a GC substrate.

4.4 Catalyst pretreatment

After the deposition of the active electrocatalyst material, the electrode surface was carefully rinsed with copious amounts of nanopure water in order to clean it from any residues of the salt bath and unattached catalyst particles. Then the electrode was placed in the electrochemical cell described in section 4.5. In order to reduce any metal oxides formed on the catalyst surface -i.e. to activate the electrocatalyst-, the sustained polarization at -1.3 V (vs. MSE) was performed for 5 minutes.

4.5 Experimental setup

A standard three-electrode, one compartment cell was used for the electrodeposition of active coatings. The counter electrode was a large-area platinum electrode of high purity (99.99%, Johnson-Matthey), which was degreased by refluxing in acetone, sealed in soft glass. The reference electrode was a commercially available saturated calomel electrode (SCE). In the case of the development of Ni-M (M = Ni, Mo, Fe, W) electrocatalysts, the working electrode was a Cu substrate of surface area 0.69 cm². While for the development of Ni/conducting polymer catalysts the working electrode was a GC substrate of surface area 0.17 cm².



Figure 4.1 Experimental setup for electrochemical measurements.

The electrocatalytic activity of the different coatings for the HER was studied in 0.5 M H₂SO₄ solution in a standard three-electrode, two compartment cell (Fig. 4.1). The counter electrode was a large-area platinum electrode of high purity (99.99%, Johnson-Matthey), which was degreased by refluxing in acetone, sealed in soft glass, and stored in 98% sulfuric acid. During the measurement, the counter electrode was a commercially available mercury/mercurous sulfate electrode (MSE). The working electrode was an electrocatalytic coating electrodeposited on a Cu substrate or on a GC substrate depending of the catalyst under study. All the measurements were carried out in an oxygen-free environment, which was achieved by continuous purging the sulfuric acid solution with argon gas.

4.6 Experimental techniques

Several experimental techniques were used to study the electrocatalytical activity of the electrodeposited coatings in the HER and to characterize the morphology, structure and chemical composition of the active coatings. The electrochemical techniques were carried out using an Autolab potentiostat/galvanostat PGSTAT 30, handled by the GPES and FRA v. 4.9 software.

4.6.1 Linear Tafel DC polarization

This technique was used to characterize the electrocatalytic activity of the prepared catalytic coatings and to derivate from the recorded curves the corresponding electrochemical parameters (Tafel slope, exchange current density, transfer coefficient).

Linear Tafel polarization was performed by polarizing the electrode under study from its open circuit potential (OCP) to the overpotential of -500 mV, using a scan rate of 0.5 mV s^{-1} . The final linear polarization curves were corrected for the IR (Ohmic) drop, based on the resistance of the electrolyte obtained from EIS measurements. All the curves were normalized to the formal potential of the H⁺/H₂ couple, taking into account the potential of the reference electrode (0.650 V *vs* NHE) and pH of the solution used (pH=0.25).

4.6.2 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is a powerful technique for the investigation of electrochemical interfaces, and processes occurring at those interfaces. It provides information about electrochemical reactions, surface coverage, conductivity, electric and dielectric properties, surface porosity and charge distribution, *etc.* EIS measurements were done in a wide frequency range from 50 kHz to 10 mHz. The *ac* voltage amplitude was ±5 mV peak to peak, and the studied overpotential range varied from the OCP to the overpotential of -500mV. The modeling of EIS spectra was done by employing Nonlinear Least Square Fit Analysis (NLSF) software [52].

4.6.3 Steady-state potential-relaxation

In order to complement the EIS results related to the determination of the true surface area of Ni/conducting polymer catalysts, the potential-relaxation technique was also used. In this technique, a specified cathodic overpotential was applied, and after the current reached a steady-state value, the polarization was interrupted. The dependence of the open circuit potential change on the time passed was then recorded.

In order to characterize the current-potential behaviour of the electrode, before performing the potential-relaxation experiments, the Tafel linear polarization was done according to the method described in section 4.6.1. After the potential-relaxation experiments, EIS measurements were performed at 2 or 3 selected overpotentials to compare the parameters calculated using the two techniques (i.e. to compare the corresponding true surface area values).

4.6.4 Characterization of the catalyst morphology, structure and chemical composition

To study the surface morphology of the Ni-M coatings, copper foils (2.5 cm long, ca. 1.2 cm wide and 0.1 cm thick) were used as substrates for the deposition of electroactive catalyst coatings. The foils were prepared according to the procedure already described in section 4.2, and nail varnish was used to cover one side of the substrate in order to have the electroactive coating deposited only on one face of the foil. Two layers of varnish were applied and the foils were left to dry overnight. The deposition conditions and salt baths compositions were the same as reported in Table

4.1. The foils were submerged around 1.2 cm in the electrolytic bath leaving an approximate area of deposition of 1.8 cm^2 .

The surface morphology of the Ni-M coatings was then observed using a Field Emission Scanning Electron Microscope (FE-SEM Hitachi 4700). In order to determine the chemical composition of the coating and to investigate the distribution of specific active elements on the coating surface, the energy dispersive spectrometry (EDS) was done using an X-Ray detector (Oxford Instruments X-Ray detector, Model 7200) interfaced to INCA 3.04 software for data display and analysis.

To obtain information on the structure of the investigated Ni-M active electrocatalyst coatings, the X-Ray diffraction analysis was done using an X-Ray diffractometer (Riaku XRD) system with a copper rotating anode at 40 kV and 120 mA. The data was exported to Microsoft Excel software for analysis. The information is reported graphically as the dependence diffracted angle *vs.* intensity and it was compared to a reference database built-in a Philips PC Identify software.

To determine the Ni-M catalyst chemical composition, an inductively coupled plasma (ICP) technique was used. The catalyst materials deposited on the copper foils were dissolved in 10 mL of boiling *aqua regia* (water, concentrated nitric acid and concentrated hydrochloric acid in a 1:1:3 volume ratio). Partial dissolution of the copper substrate was detected; however, no interference from copper was noted in the obtained values. Once the coatings were completely dissolved in *aqua regia*, the solutions were further diluted with distilled water to a total volume of 100 mL. Solutions of 50 and 100 ppm (1 mg per litter of solution) were prepared from Ni, Fe, Mo, W standard solutions (Fisher ICP standards, 1000 µg/mL) to determine a calibration curve. ICP optical emission measurements were done using a Thermo Jarrel Ash Trace Scan ICP spectrometer. Three different scans were run for each sample.

To study the morphology of Ni / CP / GC coatings only SEM technique was employed. A special GC carbon electrode of the same approximate dimensions (~0.17 cm²) as the one used in HER experiments was designed for SEM imaging. The images were taken by a Field Emission Gun Scanning Electron Microscope (FEG-SEM Phillips XL30) and its corresponding software for data display and analysis.

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CHAPTER 5

5. RESULTS AND DISCUSSION

5.1 Ni-M / Cu catalysts

5.1.1 Composition and structural characterization

Inductively coupled plasma (ICP) was used to determine the exact composition of the electrocatalyst coatings under study. The compositions of the different Ni-M catalysts (M = Mo, W, Fe) are presented in Table 3.1 in atomic %.

notation of	formula	atomic %				
catalyst	IUIIIuia	Ni	Мо	W	Fe	
Ni	Ni	100	-	-	-	
NiMo-1	Ni _{7.3} Mo	88	12	-	-	
NiMo-2	Ni₃Mo	75	25	-	-	
NiW-1	Ni _{3.4} W	77	-	23	-	
NiFe-1	Ni₄Fe	80	-	-	20	
NiFe-2	NiFe _{5.6}	15	-	-	85	

Table 5.1 Chemical composition of electrocatalysts obtained by an ICP analysis.

In order to investigate the influence of the catalyst composition on the hydrogen evolution, an attempt to produce two different alloy compositions was made, by changing the electroplating bath compositions (Table 4.1). From Table 5.1 it can be observed that the largest difference in the composition ratio was achieved for the NiFe coating. In the case of NiMo, two different alloy compositions were obtained; however, both of them were richer in nickel. For NiW it was possible to produce only one composition of the coating. A relevant change in the bath composition on the account of increased W content (W / Ni = 3) did not result in any significant increase in the content of W in the coating.

X-ray diffraction (XRD) was used for the structural characterization of the Ni-M catalysts. The diffraction patterns are shown in Figure 5.1. The range of variation of the diffraction angle was $30^{\circ} < 2\theta < 100^{\circ}$. The spectrum recorded on pure Ni shows that the coating is crystalline. The peaks recorded correspond in increasing order of 2θ to the

(111), (200), (220), (311) and (222) reflections of the f.c.c. structure of the nickel [53]. Contrary to the nickel coating, the spectra on NiMo show the halo pattern indicating the existence of amorphous structure [54]. The NiMo coating with a higher content of nickel (NiMo-1) shows broad peaks corresponding, in increasing order of 2θ , to the (111), (200), (220), (311) and (222) reflections of the f.c.c. structure of the nickel phase supersaturated with molybdenum [55]. Hence, NiMo-1 coating can be regarded as a solid solution with an f.c.c. nickel-rich structure (known as the α phase) with molybdenum atoms subsitutionally dissolved in nickel. The NiMo-2 coating shows even a larger degree of amorphous structure, with Ni (220) reflection almost, and (311) and (222) completely absent. The increase in a degree of amorphousness (*i.e.* peak broadening) with the increase in Mo content has also been observed by Highfield *et al.* [17].



Figure 5.1 X-ray diffraction (XRD) patterns of Ni-M coatings electrodeposited on a Cu substrate.

Similarly, the spectrum recorded on NiW-1 shows a single f.c.c. nickel phase saturated with tungsten. However, in this case, the peaks are quite defined (narrow) indicating that this coating is a solid solution of tungsten in nickel that consists of

tungsten atoms substitutionally dissolved in the f.c.c. structure of nickel [53]. The spectrum also demonstrates that the coating is crystalline. In the case of the NiFe-1 coating, the broad Ni (111) peak again indicates the existence of an amorphous pattern, with Ni (200), (220), (311) and (222) reflections completely absent. This is in contrast to the results of Cheung *et al.* [56], whose XRD analysis confirmed that a NiFe alloy of a very similar composition (22.2% Fe) obtained by electrodeposition was completely crystalline. In contrast to NiFe-1, the NiFe-2 coating shows a well-defined Ni (111) peak indicating that the material is of a crystalline structure.

The absence of the other Ni diffraction lines in all the samples indicates that, during the preparation of the coatings, the nucleation of other phases did not take place. Hence, the main phase in all the coatings is the nickel f.c.c. structure, with the second element incorporated into the structure.

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5.1.2 Morphology of the electrodes

In order to examine the morphology of the electroactive coatings used in research, scanning electron microscopy (SEM) was used. The SEM images in Figure 5.2 show significant differences in morphology between the investigated catalytic coatings. The pure nickel electrode (Figure 5.2a) shows a relatively homogeneous surface of a small roughness, which thus can be considered as a quazi-two-dimensional surface. The morphology of the surface is in accordance with the crystalline structure obtained by the XRD analysis, and the micrograph taken at a higher magnification showed polygonal forms, characteristic of a crystalline structure. On the other side, from Figure 5.2b and 5.2c it can be observed that the NiMo samples show spherical (globular) and cauliflowerlike pattern having considerably rougher surface than pure nickel. The size of the globules is smaller for the NiMo-2 sample, which contains less nickel. It can also be observed on both micrographs that some smaller ellipsoid-shaped globules appear on top of the larger globules. The borders of both smaller and bigger globules are circular or quazi-circular, which is quite different than the polygonal form of polycrystals observed on nickel, indicating the absence of grain boundaries, thus supporting the XRD spectra that show the amorphous structure of both NiMo coatings. The micrograph of the NiMo-1 coating shows that the coating is very porous and of a three-dimensional structure, thus indicating a high surface area available for the HER reaction. The micrograph of the NiW-1 electrode (Figure 5.2d) shows the presence of cracks on a relatively uniform surface, and no grains of any type could be observed even at high magnifications. A similar uniform surface can also be seen in Figure 5.2e for NiFe-1 alloy. However, in this case small irregular grains started to form on the surface. On the other hand, the coating with the higher content of iron (NiFe-2, Figure 5.2f) shows a quite different structure where small, well-distributed grains can be observed on the whole surface. The SEM images taken at higher magnifications showed that the grains are star-shaped, with the average size of ca. 200 nm. This is in agreement with the XRD spectrum (Figure 5.1) that showed the crystalline structure of the NiFe-2 coating.



In addition to the SEM images, energy dispersive spectrometry (EDS) was used in order to determine the chemical composition of the coatings and to investigate the distribution of the elements on the electrode surface (graphs not shown here). All the EDS spectra showed the characteristic peaks for nickel and the alloying elements, which is consistent with the ICP results already discussed. The surface mapping of Ni and the alloying elements confirmed a very uniform distribution of the elements on the surfaces of all coatings, which is one of the major conditions that has to be fulfilled when designing a multicomponent electrocatalyst.

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5.1.3 Linear Tafel polarization

In order to characterize electrocatalytic activity of the prepared catalytic coatings Tafel linear polarization measurements were made, and the corresponding electrochemical parameters (Tafel slope, exchange current density, transfer coefficient) were derived from the recorded curves. To understand this electrochemical technique a brief theoretical explanation is given in the following paragraphs.

When mass transport is not a factor determining the current and instead it is controlled only by charge transfer, the current density can be related exponentially to the overpotential η . This relation was expressed by Tafel in 1905 as [48],

$$\eta = \frac{2.303RT}{n\beta F} \log j_0 - \frac{2.303RT}{n\beta F} \log j$$
 (5.1)

But for practical proposes Tafel equation is generally written as

$$\log j = \log j_0 - \frac{2.303RT}{n\beta F}\eta$$
(5.2)

where *j* is the current density (A cm⁻²), j_0 is the exchange current density (A cm⁻²), β is the symmetry factor (dimensionless), *n* represents the number of electrons exchanged, *F* the Faraday constant (= 96485 C mol⁻¹), *R* the gas constant (= 8.314 J mol⁻¹ K⁻¹), *T* the temperature (*K*) and η the applied overpotential (V). The exchange current density j_0 is a characteristic kinetic parameter of an electron transfer process when no net current is flowing (equilibrium condition) and there is no overall chemical change in the cell. The parameter β represents a fraction (0 to 1) of the total energy supplied that is used to lower the activation energy of the reaction. The overpotential η is the applied current to deviate the potential from the equilibrium value and *j* is the resulting (measured) current density. The current is directly related to the amount of hydrogen produced. Furthermore, small values of η that yield high values of *j* are always desired because a small energy input would generate a high amount of H₂.

A plot of log *j* vs. η , is a useful device for evaluating kinetic parameters because the value of the exchange current density (*j*_o) can be obtained directly from the intercept on the current axis and the symmetry factor (β) can be calculated from the slope (*b*) of the graph:

$$b = \frac{2.303RT}{n\beta F} \tag{5.3}$$

Since mass transfer effects are absent, the overpotential associated with any given current is thus directly related to the change in activation energy. It is required to drive the heterogeneous process at the rate reflected by the current. The lower the exchange current, the more sluggish are the kinetics at an equilibrium condition; hence, the larger is the electrode activation overpotential required for any particular current. If j_{o} is very large, then the system can supply large currents with insignificant activation overpotential. The exchange current can be viewed as a kind of "idle speed" for current exchange across the interface, and it is a measure of any system's ability to deliver a net current without a significant energy loss due to activation [48]. For those reasons, the exchange current has been used as one of the ways to express the intrinsic electrocatalytic activity of an electrocatalyst, and a high value is always desired. However, it has been shown more recently that the value of Tafel slope is equally -if not more- important in the characterization of the catalyst intrinsic activity [24]. The other parameter that characterizes a catalyst is the asymmetry factor (β). It represents a fraction of the total energy supplied that it is used to lower the activation energy of the reaction as mentioned before, and, naturally, a higher value of β is desirable. Since the Tafel slope (b) is inversely related to β , a low value of b is preferred -i.e. characterizes a better electrocatalyst.

The Tafel polarization curves for hydrogen evolution in 0.5 M H₂SO₄ on Ni and Ni-M alloys (M = Mo, W, Fe) are presented in Figure 5.3. The curves are corrected with respect to the thermodynamic HER potential (formal HER potential) at the given conditions and for the IR drop. The first observation is that the OCP on the Ni, NiMo and NiW is ca. 40 mV, or 220 mV and 130 mV for NiFe-1 and NiFe-2, respectively, more negative than the thermodynamic H⁺/H₂ potential -0.015 *vs.* NHE in 0.5M H₂SO₄, pH = 0.25. By comparing these values to the thermodynamic values related to the most negative potential, one can get some indication of the presence of oxide films on the catalyst surface. The most negative values correspond to the oxidation of Ni, Mo, W and Fe to their first oxidation ionic state or oxide state [57]. The OCP values for the

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investigated coatings (Figure 5.3) are ca. 220 mV (Ni), 170 mV (NiMo-1 and NiMo-2), 100 mV (NiW-1), 311 mV (NiFe-1) and 230 mV (NiFe-2) positive to the corresponding thermodynamic potentials for the oxidation of the metals to Ni²⁺, Mo³⁺, WO₂, and Fe²⁺. This indicates that each coating is at the OCP covered by a thin oxide film that protects the coating component(s) from further dissolution (corrosion), thus making the OCP more positive than the corresponding thermodynamic oxidation potential. Similar observations have been already reported on Ni-based catalysts [17,23,58]. From the relative difference in the above values one can speculate that the least compact (protective), oxide film is formed on NiW-1, while the most protective film is formed on NiFe-1. The cathodic polarization of the coatings may reduce some of the oxide films completely to the metal, but the present results do not give sufficient information to support this conclusion.



Figure 5.3 Linear Tafel polarization curves for different Ni-M (M = Mo, W, Fe) electrocatalysts.

The Tafel curve recorded on pure Ni (Figure 5.3) shows a classical Tafelian behavior; it clearly indicates that the HER on Ni is a purely kinetically controlled reaction that can be described using the Tafel equation (Eq. (5.2)). Since the Ni curve in Figure 5.3 does not show any significant change in the slope, the same HER reaction

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mechanism is valid through the entire overpotential region investigated. The value of the Tafel slope is 147 mV decade⁻¹. According to the general models for the HER mechanisms in the acidic media [48,59,60], if the Volmer reaction step -i.e. adsorption of hydrogen (Eq.(2.5))-, is rate determining, a resulting Tafel curve should yield a slope of 116 mV decade⁻¹ at 20°C. If the electrochemical desorption step, Heyrovsky step, is rate determining (Eq.(2.6)), the measured Tafel slope would yield a value of about 40 mV decade⁻¹, or 30 mV decade⁻¹ for the Tafel desorption step (Eq.(2.7)) -*i.e.* chemical desorption. Hence, the Ni curve in Figure 5.3 clearly demonstrates that the hydrogen evolution on Ni is controlled by the Volmer reaction step -i.e. the adsorption of hydrogen to form Ni-H. It could also be noticed that the measured Tafel slope value slightly deviates from the theoretical value in a positive direction. This phenomenon has already been reported in the literature [23,29,61], but the fundamental explanation of the reason of its appearance has not been always given. As previously discussed in the text, it appears that the Ni coating is covered by a thin layer of nickel oxide. Consequently, the presence of this thin surface oxide film could be related to the increased Tafel slope value (Figure 5.3). Since Ni-oxide is a semiconductor, its electronic conductivity is lower than the conductivity of pure metallic Ni -i.e. the electron transfer thorough the nickel oxide film is slightly impeded. This is, in turn, related to the symmetry factor, β , the value of which then decreases, thus producing an increase in Tafel slope, assuming that the reaction mechanism does not change (for the Volmer step as the rds, the symmetry factor, β , is equal to the transfer coefficient, α , while for the Heyrovsky step as the rds, the transfer coefficient is $\alpha = 1 + \beta$ [48]). Basically, due to the decrease in the electron conductivity through the thin oxide layer on the catalyst surface, the external energy invested through the application of overpotential is used not only for the HER, but also to overcome an electron transfer barrier located inside the thin oxide film (band gap), on the account of a lower decrease in the HER activation energy -i.e. lower transfer coefficient value ($\alpha_{Ni} = \beta_{Ni} = 0.4$, Table 5.2). From this perspective it is obvious that the ratio of the invested energy that is distributed between the HER and electron transfer inside the oxide film, depends on the electric/dielectric properties of the film and its thickness. Metikos-Hukovic et al. [21] have reported an enormously high Tafel slope 667 mV decade⁻¹ for the HER on pure zirconium in 1M NaOH, and explained it on the basis of the presence of a thick barrier-type Zr-oxide film on the catalyst surface. However, much lower values have been reported on Ni and Ni-based alloys [23,29,61]. From the

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discussion above one can conclude that a higher value of transfer coefficient, α , indicates better electrocatalytic activity, which is often used as a comparison parameter.

In contrast to pure Ni, the polarization curves recorded on the bicomponent electrocatalysts (Figure 5.3) display two potential-dependent regions of the HER behavior. At low overpotentials the curves display a well defined Tafelian behavior, with an exception of NiFe-2. The latter also shows two regions of different behavior, but the high-overpotential region is more defined in terms of the Tafelian behavior. Nevertheless, all the curves demonstrate that at higher overpotentials a significant deviation from the low-overpotential Tafelian behavior was recorded *-i.e.* a change in the Tafel slope. These two regions are named as "Region I" and "Region II", and the electrochemical parameters derived from the curves in Figure 3 for both regions are presented for each alloy in Table 5.2. The deviation from the Tafelian behaviour at high overpotentials or even the existence of two-Tafel-regions has already been reported in the literature [17,24,55,58,63-65] for similar HER electrocatalytic materials. This point will be discussed shortly in the text in relation to the behavior observed at high overpotentials (Figure 5.3).

	R	egion I	Region II		
Catalyst	<i>b</i> (mV decade ⁻¹)	<i>j₀</i> (µA cm ⁻²)	α	<i>b</i> (mV decade ⁻¹)	α
Ni	147	-2.6	0.39	119	0.49
NiMo-1	38	-20.5	1.53	118	0.49
NiMo-2	40	-12.4	1.45	123	0.47
NiW-1	43	-10.3	1.35	116	0.50
NiFe-1	94	-2.0	0.62	160	0.36
NiFe-2	86	-0.4	0.67	146	0.40

Table 5.2 HER kinetic parameters obtained by the analysis of the Tafel curves presented in Figure 5.3.

The curves presented in Figure 5.3 show that in the low current density region (region I), Tafel slope values for NiMo-1, NiMo-2 and NiW-1 are between 38 and 43 mV decade⁻¹. Similar values were also obtained on sputter-deposited NiMo and NiW coatings in a highly basic medium [55], and NiMo electrodes prepared by arc-melting [17] in a highly acidic medium. According to the previous discussion of the relation

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between the Tafel slope value and corresponding rds reaction step, it appears that the Heyrovsky desorption step Eq.(2.6) controls the HER kinetics on these electrocatalysts at low overpotentials, while the Volmer step, Eq.(2.5) occurs at a significant rate. For NiFe-1 and NiFe-2 electrocatalysts, the Tafel slope at low overpotentials is of a higher magnitude, 94 and 86 mV mV decade⁻¹, respectively. These values are slightly lower than the value characterizing the Volmer reaction as the rds (116 mV decade⁻¹), but significantly higher for the value characterizing the Heyrovsky step (40 mV decade⁻¹). The corresponding transfer coefficients are 0.62 and 0.67. Larger transfer coefficient would indicate better electrocatalytic activity, but Figure 5.3 shows that a large overpotential is required to start evolving hydrogen on the NiFe catalysts, while all other coatings require much lower overpotentials. This was already discussed in terms of the existence of an oxide film on the NiFe surface, which inhibits the electron-transfer, and consequently larger overpotentials are required for the HER to occur. In addition, the EIS measurements showed that the NiFe coatings express different impedance behavior than the other coatings, which is most likely influenced by the existence of an oxide film on the coating surface (this will be discussed later in the text). Taking this discussion into account it seems that the rds on the NiFe coatings is the Heyrovski step. This is also supported by the results in [24] where two Tafel regions were also recorded, but the slope of the Tafel region at low overpotentials was ca. 40 mVdecade⁻¹, indicating the Heyrovsky step as the rds on NiFe coatings. However, it has to be emphasized that the measurements presented in paper [24] were done at very high pH values (1M KOH).

Figure 5.3 shows that with the increase in overpotential there is a change in the Tafel slope on all the bimetallic electrocatalysts studied. In the high overpotential region (Region II), NiMo-1, NiMo-2 and NiW-1 electrocatalysts yielded a Tafel value ca. 120 mV decade⁻¹ (see Table 5.2), which is in a very close agreement with the values obtained on sputter-deposited NiMo and NiW electrodes in a highly basic medium (1M NaOH) [55] and arc-melted NiMo electrodes in an acidic medium [17]. The values reported on the Ni-Fe catalysts are somewhat higher, which is in accordance with the previous discussion related to the Tafel behavior in Region I. On the other side, the Tafel value obtained on pure nickel decreased to 119 mV decade⁻¹, which indicates that the thin nickel-oxide film present at the OCP and low overpotentials was removed (reduced) during the cathodic polarization at high overpotentials, thus increasing the symmetry factor β (or transfer coefficient, α , in this case since $\alpha = \beta$). Similar assumption was also reported in [17].

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The change (decrease) in the Tafel slope with polarization has also been reported in the literature [17,21,24,55,58,63-66], and many explanations have been given. One of the explanations for the observed behavior is the change in the reaction mechanism -i.e. the transition from the Heyrovsky to the Volmer rds [17]. This could be related to the depletion of the d-electron density at the Fermi level of the alloys by adsorbed hydrogen [68], which remains partially uncompensated at lower overpotentials. However, by cathodic polarization to higher overpotentials, the *d*-electron density increases at the Fermi level, which can improve the kinetics of the Heyrovsky step, and the Volmer step becomes the rds at high overpotentials. Another possible explanation for the observed Tafel slope change can be related to the influence of uncompensated ohmic drop [66]. However, the curves presented in Figure 5.3 were corrected for the IR drop and the latter possibility can thus be eliminated as a reason for the observed change in Tafel slopes at high overpotentials. Although the limiting current for the HER is very high (7 Acm⁻²) [65], a possibility of mass-transport limitations, through narrow pores on the catalyst surface, could be yet another possible reason for the observed diffusionlike shapes of the Tafel curves on bimetallic coatings (Figure 5.3) [63]. However, the EIS analysis did not show the existence of mass-transport limitations, and this possibility can also be dismissed. An another explanation could be that the Tafel slopes observed at very high overpotentials can be related to the formation of hydrides in the surface layer [21,24,17]. By polarization of the surfaces to high overpotentials, a large amount of atomic and molecular hydrogen is generated, and the bimetallic coatings can absorb this hydrogen present at the catalyst surface. The strong bonding between metal and absorbed H atoms becomes a barrier to hydrogen evolution, due to the modification of the electronic and structural properties of the coating in the near-surface region, thus influencing the increase in the Tafel slope and hydrogen overpotential at high current densities. Yet another possible explanation for the observed change in the Tafel slope is related to the decrease in the active surface-area [66,58,64]. Marrozi et al. [64] postulated that at high overpotentials occlusion of hydrogen inside the pores occurs. This, in turn, blocks the available surface area for the reaction, resulting in the decrease of the current density at a particular overpotential. As it will be shown later in the EIS section, only the NiFe coatings show the susceptibility towards the surface blockage, and hence the latter explanation can be used as one of the factors that contributes to the change in the Tafel slope on the NiFe coatings (Figure 5.3). Due to the electron-donor

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character of hydrogen, going from the right-hand side transition metals with almost-filled d-orbitals (e.g. Ni) to the left-hand side metals with half-filled or almost-empty d-orbitals (e.g. Mo, W, V, Ti), the binding energy for an M-H bond increases [36], and thus the metal's ability to form corresponding hydrides. Hence, it can be expected that the bimetallic coatings used here (especially NiMo and NW) are more susceptible to hydride formation than pure nickel. This susceptibility increases with an increase in cathodic (over) potential. Therefore, the formation of hydrides at high overpotentials seems to be the major reason for the change in the Tafel slopes recorded on the bimetallic coatings, especially on NiMo and NiW, but the change in the d-electron density and subsequent influence on the kinetics of the Heyrovsky reaction step can also be a contributing factor.

Considering the exchange current density values (j_o) presented in Table 5.2, we can see that the highest value is given by NiMo-1 (assuming the extrapolation is done with respect to the thermodynamic potential, *i.e.* zero overpotential), indicating that this catalyst is thermodynamically the most active among the catalysts investigated. The other two bimetallic catalysts, NiMo-2, NiMo-2 also show a better performance when compared to pure Ni, while the NiFe catalysts seem to be less active. Although the value of the exchange current density is very frequently used for the characterization of the electrocatalytic activity, it has been reported that a value of the Tafel slope in the low overpotential region (i.e. the high value of transfer coefficient) is as, or even more, important than a favorable j_0 [24]. This is due to the fact that the HER reaction does not occur at the thermodynamic potential (zero overpotential), but at a certain overpotential value. Hence, in order to compare the electrocatalytic activity of the catalysts better in Figure 5.3, one can fix the current density value (*i.e.* hydrogen "production" rate) and compare the resulting overpotentials required to reach the give current density. This would give an indication of the amount of energy (overpotential) that has to be invested to produce a fixed amount of hydrogen, since the current is directly related to de amount of hydrogen produced. The overpotential values for each catalyst at a fixed current density of 1 mA cm⁻² are presented in Table 5.3, along with the corresponding power values.

	<i>j</i> = 1 mA	∖ cm ⁻²	η = -150 mV		
Catalyst	η	Power	j	Volume of H ₂	
	(mV)	(mW)	(mA cm ⁻²)	(Lh ⁻¹)	
Ni	-379	0.379	-0.027	6	
NiMo-1	-65	0.065	-56.350	12638	
NiMo-2	-75	0.075	-22.900	5136	
NiW-1	-85	0.085	-10.440	2341	
NiFe-1	-257	0.257	-0.062	14	
NiFe-2	-284	0.284	-	-	

Table 5.3 Comparison of the electrocatalytic activity of the investigated catalyst coatings in terms of (*a*) the overpotential and power input needed for a fixed hydrogen production rate, determined by the current density of 1 mA cm⁻², and of (b) the resulted production rate at a fixed energy input (fixed overpotential of -150 mV).

From the table it is obvious that Ni requires the largest energy input for the given hydrogen production rate (-0.379 V or 0.379 mW), while NiMo-1 requires the lowest energy input (-0.065 V or 0.065 mW), -i.e. almost six times lower energy input then pure nickel. Another common way used to compare the electrocatalytic activity of HER electrocatalysts is to fix the overpotential (energy input) and compare the resulting current densities -i.e. the amount of hydrogen that would be produced by each catalyst. In order to illustrate better the difference between the electrocatalysts investigated, the calculations for the hydrogen production at a fixed overpotential of 150mV in an imaginary PEM H₂ generator of 50 membranes, each 1 m² of geometric surface area operating at standard conditions are also presented in Table 5.2. Again, similarly to the behaviour obtained at a fixed current density, NiMo-1 yields the best electrocatalytic activity -i.e. the amount of hydrogen that could be produced using NiMo-1 is ca. 2100 times larger than if pure Ni is used. In conclusion, the trend in electrocatalytic activity presented in Table 5.2 is the same as the trend already observed on the basis of the exchange current density, and shows that the HER electrocatalytic activity of the investigated catalysts decreases in the direction of NiMo-1 > NiMo-2 > NiW-1 > NiFe-1 > Ni > NiFe-2. This procedure is commonly used in the literature for the comparison of HER catalysts.

The information obtained from the Tafel polarization data demonstrates that all Ni-M catalysts are very active for the HER, showing much better *overall* catalytic activity than pure Ni. NiMo-1 has shown to be the best overall catalyst. However, since the Tafel curves presented in Figure 5.3 are normalized to the *geometric* area of the catalyst, not

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to the real electrochemical area, the results discussed above cannot offer a definite conclusion if the observed electrocatalytic activity is a result of the increased surface area of the catalyst only, or better intrinsic (electronic) electrocatalytic properties of the catalyst material, or the combination of the two. Thus, in order to investigate which of the electrocatalystis is intrinsically the best material for the HER, the curves presented in Figure 2 should be normalized to the true, electrochemically active surface area of the electrocatalyst. Some initial conclusion can be made on the basis of SEM images (Figure 5.2), where it is obvious that the NiMo-1 surface shows the highest surface roughness. This is also consistent with the results presented in Figure 5.3. However, the increase in an electrode surface area that can be observed by SEM imaging, does not have to be necessarily in direct correlation with the increase in the *electrochemically active* surface area. Thus, an electrochemical technique is needed to determine the actual active surface area of the electrode coating. There are several techniques that can be used to determine a true surface area of a catalyst. Recently some of them have been discussed in [21,69,70], and EIS technique was proposed as the most appropriate technique that can be used for the true surface area determination in electrochemical systems. Thus, the following section of the thesis will discuss the EIS results obtained on all the catalytic coatings used. Some of the parameters calculated will then be used in order to evaluate the true electrochemically active surface area of the catalyst, which will enable us to compare the intrinsic electrocatalytic activity of the materials investigated.

5.1.4 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is a powerful technique for the investigation of electrochemical interfaces, and processes occurring at those interfaces. It provides information about electrochemical reactions, surface coverage, conductivity, electric and dielectric properties, surface porosity and charge distribution, etc. In this work the EIS technique was applied to further investigate the electrode/electrolyte interface and the corresponding processes that occur at the electrode surface. To ensure complete characterization of the electrode/electrolyte interface and corresponding processes, EIS measurements were made over six frequency decades, from 10 kHz to 10 mHz at selected overpotentials over the whole range covered in the Tafel plots (ca. from the OCP to the potential of OCP-500 mV). Figure 5.4 shows an example of EIS spectra recorded on the NiW-1 electrocatalyst at several selected overpotentials. The presentation of the data in form of a Bode impedance plot (Figure 5.4b) clearly reveals the presence of three distinguishable frequency-dependent segments, which is most evident on the spectrum recorded at the lowest overpotential. In the high-frequency region (HF) -i.e. above ca. 400 Hz- the absolute impedance curve is almost independent of frequency, with the phase angle value approaching zero degree. This is a typical response of a resistive behavior and corresponds to the ohmic resistance of the electrolyte between the working and reference electrode. The lower-HF region, between ca. 100 and 2 Hz, can be related to the fast charging/discharging process at the electrode electrolyte interface [48,72,73] governed predominantly by a capacitive behavior that is characterized on the graph with the first phase angle maximum of ca. 42° at 4 Hz. This lower-HF region represents a response of a system characterized by a time constant, τ_1 . At frequencies below ca. 1 Hz (low-frequency region, LF) the influence of a second time constant, τ_{2} , appears. The phase angle reaches a second maximum of ca. 57° at 140 mHz, below which it starts to decline, while the absolute impedance curve slope also starts decreasing. If one made the measurement to even lower frequencies, the leveling of the absolute impedance curve would be seen, indicating a pure resistive response of the system (so-called dc limit). This is also supported by the Nyquist plot (Figure 5.4a), where a LF semicircle (larger semicircle) is not completely closed, but clearly shows a regular closing tendency towards the real impedance axis. This is a typical behavior characteristic for an electrochemical system controlled by a resistive component. In order to demonstrate that all the catalytic coatings investigated express a

two-time-constant behaviour seen in Figure 5.4, a Nyquist plot of each of the catalyst is presented in Figure 5.5.



Figure 5.4 Nyquist (a) and Bode plots (b) recorded at different HER overpotentials on NiW-1 electrocatalyst. Symbols are experimental data and solid lines are fitted data.



Figure 5.5 Nyquist plots for Ni-M coatings recorded at (Ni) 45 mV, (NiMo-1) 45 mV, (NiMo-2) 45mV, (NiW-1) 35 mV, (NiFe-1) 160mV, and (NiFe-2) 225 mV. The plots show a two-time-constant response. Symbols are experimental data, while solid lines represent a response of a system characterized by one time constant and are shown in order to aid the visual distinction of two time constants on experimental plots.

The plots in the figure show that the two-time-constant response is clearly visible either as a definite appearance of two semicircles (NiMo-1, NiMo-2, NiW-1 and NiFe-1) or as a broadened (distorted) semicircle on Ni and NiFe-2. The zoomed insets in Figure 5.5 are added to demonstrate this more clearly; and in the case of Ni and NiFe-2, a modeled one-time-constant response is presented as a solid line to demonstrate the distortion of the semicircle. At the moment it is important to note that the plots presented in Figures 5.4 and 5.5 clearly show the existence of two time constants, which is used as a basis for the modeling of the EIS spectra. The relation of the time constants to specific surface processes will be discussed later in the text.

In order to obtain a physical picture of the electrode/electrolyte interface and the processes occurring at the catalyst surface, the experimental data were fitted using nonlinear least-squares fit analysis (NLLS) software [52] and an electrical equivalent circuit (EEC). Three different ECC models described in the literature [23,29,74] have been used to explain the *ac* impedance of the HER on nickel-based electrodes (Figure 5.6): (1) one-time constant model (1T), (2) two-time constant parallel model (2TP), and (3) two-time constant serial model (2TS). In the absence of the response related to the hydrogen adsorption, the 1T model describes the response of the HER on relatively smooth surfaces [21], or surfaces containing narrow and wide cylindrical pores where the signal penetrates up to the bottom of the pores, and the electrode resembles the behavior of a flat one [75,76]. The same model was also used by Savadogo and Ndzebet [77] to model the EIS spectra for the HER on Pt-Co alloy supported on carbon and electroactivated by $SiW_{12}O_{40}^{4-}$.

The 2TP model (Figure 5.6b), which represents slightly modified model originally proposed by Armstrong and Henderson [78], has been used most frequently to describe the response of the HER on both porous [24,75,79] and smooth electrodes [80,81]. It reflects the response of the HER system characterized by two time constants, both of them related to the kinetics of the HER. It has been postulated that the first time constant, τ_1 (CPE₁-R₁ Figure 5.6b), is related to the charge transfer kinetics, while the second time constant, τ_2 (CPE₂-R₂), is related to the hydrogen adsorption. Both time constants change with overpotential.

The 2TS (Figure 5.6c) model has also been used to describe the response of the HER on porous electrodes [23,59,75]. Similarly to the 2TP model, it reflects the response of the HER system characterized by two time constants, but only one of them (τ_1 , CPE₁-R₁) is related to the kinetics of the HER. This time constant changes with overpotential. The other time constant (τ_2 , CPE₂-R₂) is related to the porosity of the electrode surface, and does not change with overpotential. Hence, this can be used as a criterion to prescribe the EEC parameters to the specific processes (*i.e.* charge transfer kinetics, surface porosity or hydrogen adsorption).



Figure 5.6 Different ECC models commonly used to explain the EIS response of the HER on nickel-based electrodes: (a) one-time constant model (1T), (b) two-time constant parallel model (2TP), and (c) two-time constant serial model (2TS).

Figure 5.4, that shows an example of EIS spectra recorded on a NiW-1 coating at several selected overpotentials, and the Nyquist plots in Figure 5.5, clearly show the response of a system characterized by two time constants. Therefore, in order to model the experimental data on NiW-1 both two-time constant EEC models were tested *-i.e.* the 2TP and 2TS EEC models (Figure 5.6). Figure 5.4 shows that a very good agreement between the experimental data (symbols) and simulated data (solid line) was obtained when the parallel EEC (2TP) model was used. The use of the serial model (2TS) resulted in a large disagreement between the experimental and simulated data for Ni, NiMo-1, NiMo-2 and NiW-1. However, the 2TS model was successfully used to fit the EIS spectra on NiFe-1 and NiFe-2 coatings. The EEC parameters obtained by modeling

of the investigated coatings at all the applied overpotentials are presented in Table 5.4 at the end of this section. Further, the fitting procedure showed that a better agreement between theoretical and experimental data was obtained when pure capacitance in the model was replaced by a frequency-dependent constant phase element (CPE). Generally, the use of CPE is required due to a distribution of the relaxation times as a result of inhomogeneities present at a microscopic level [72]. Initially this has been contributed to the surface roughness/porosity [82], or an interface that can be described by either a fractal geometry concept or an RC transmission line concept [83]. On the other side, a recent study [84] has attributed the presence of the CPE to atomic scale inhomogeneities, rather than to the geometric aspects of the surface in terms of its roughness. However, initial explanation can be rationalized alternatively in such a way that increasing roughness may broaden the time constant distribution of adsorption kinetics, and may therefore increase the capacitance dispersion, requiring thus the use of a CPE [85]. Indeed, our measurements on various electrochemical systems support the above explanation that the deviation from the purely capacitive behavior does not have to be necessarily related to the surface roughness, but could appear as a result of adsorption of ions and molecules at the electrode/electrolyte interface. The CPE can also include contribution from a dynamic disorder such as diffusion [86]. The impedance of a constant phase element is defined as [52]:

$$Z_{CPE} = [CPE(j\omega)^n]^{-1}$$
(5.4)

with $-1 \le n \le 1$, where Z_{CPE} ($\Omega \text{ cm}^2$) is the impedance of a constant phase element. The constant CPE ($\Omega^{-1} \text{ s}^n \text{ cm}^{-2}$ or F s^{*n*-1} cm⁻²) is a combination of properties related to both the surface and the electroactive species and it is independent of frequency. The exponent *n* is related to the slope of the log*Z* against log*f* Bode plot *-i.e.* to the phase angle θ by the relation $n = 2\theta/\pi$ and $j = -1^{0.5}$. A pure capacitance yields n = 1, a pure resistance yields n = 0, a pure inductance yields n = -1, while n = 0.5 or 0.25 represents the Warburg diffusion impedance. In some cases, if the surface is porous and the adsorption of electroactive species occurs, *n* can decrease to very low values (e.g. for NiFe-1 it was as low as 0.2 at low overpotentials, Table 5.4), but still cannot be related to the diffusion effects, but rather to the high dispersion of (pseudo)capacitance. The CPE approach was used to fit the EIS experimental spectra on the bicomponent catalysts (NiMo, NiW and NiFe), while the fitting procedure on pure nickel showed that the exponent of CPE₂

element (Figure 5.6b) gave the value of unity. Hence, in this case the CPE_2 element was replaced by pure capacitance, *C*.

An example shown in Figure 5.4 demonstrates that as the overpotential increases, there is a significant change in the impedance response. The Nyquist complex-plane plot (Z'' vs. Z') shows two quite distinguishable semicircles (*i.e.* two time constants) at low overpotentials. With the increase in overpotential the overall 'diameter' of the semicircles decreases, indicating a significant change (i.e. enhancement) in the HER kinetics, which is characterized by the value of real impendence (the intersection of the low-frequency, LF, semicircle with the real impedance axis). The graph scale, determined by the spectra recorded at the lowest overpotential, does not allow a clear trend in the high-frequency (HF) semicircle to be observed, and it seems as the HF semicircle disappears with increasing overpotential. However, at the same time the Bode plot (Figure 5.4) clearly shows the existence of two time constants at all overpotentials presented. Hence, by visual inspection it is not possible to determine clearly the trend of the two time constants with overpotential. Therefore, a better approach is to inspect the data in Table 5.4 and conclude on the trend in the overpotential behavior. This is quite necessary in order to explain the situation reflected by the recorded EIS spectra -i.e. to relate the two time constants to specific physical phenomena (charge-transfer kinetics, hydrogen adsorption, surface porosity). Studies of the HER on solid electrodes [23,59,75] have shown that when the radius of the semicircle at high frequencies (Figures 5.4 and 5.5, smaller semicircle) is practically potential-independent, it can be related to the electrode surface porosity response, while the potential-dependent semicircle at low frequencies (Figures 5.4 and 5.5, larger semicircle) can then be related to the charge transfer resistance process. In this case, the lower value time constant (HF constant) represents the response of surface pores, while the higher value time constant (LF constant) is then related to the HER kinetics. On the other hand, when both semicircles -i.e. both time constants change with overpotential-, then one time constant can be related to the response of hydrogen adsorbed on the electrode surface, while the other one represents the HER kinetics [24,75,79-81]. In this case, the time constant related to the charge transfer resistance is usually much smaller than that for the adsorbed hydrogen. Hence, the response of the former appears in the high frequency region while the response related to the adsorbed hydrogen appears at low frequencies. Defining the possible combinations of time constants and having those related to specific

surface phenomena, it is now easy to investigate the situation on the catalysts presented here and to get a clear picture about the processes occurring on their surfaces.

The EEC parameter values presented in Table 5.4 show that both time constants (τ_1 , CPE₁-R₁, and τ_2 , CPE₂-R₂ or C-R₂ for Ni) change (*i.e.* decrease) with overpotential. Hence, none of them can be related only to the surface porosity. The value of CPE₁ is relatively constant, with very small standard deviation. On the other hand, the value of resistance R_1 decreases rapidly with an increase in overpotential. Hence, on the basis of the behavior of these two parameters with overpotential, one can conclude that the first time constant, τ_1 (CPE₁-R₁) can be related to the HER charge-transfer kinetics, namely to the response of the double layer capacitance, CPE₁, and charge transfer resistance, R_1 . Contrary to the behavior of CPE₁, the table demonstrates that the value of CPE₂ (or C for Ni) changes significantly with overpotential. In the case of Ni, NiMo and NiW, with increase in overpotential the value of C or CPE_2 also increases. At the same time the value of R_2 decreases. This is a typical behavior related to the response of hydrogen adsorbed on the electrode surface, namely to the hydrogen adsorption pseudocapacitance, CPE_2 (or C) and resistance, R_2 [24,75,79-81]. It is evident from Table 5.4 that the time constant related to the hydrogen adsorption response on Ni, NiMo and NiW surfaces, τ_2 , is higher than the time constant related to the HER chargetransfer kinetics, τ_1 , which is in accordance with the previously discussed relation between the two semicircles (Figures 5.4 and 5.5), relating EEC parameters (Figure 5.6), and their corresponding frequency domains.

However, the EIS behavior of the NiFe coatings is more different than the behavior of other four coatings. Firstly, the use of the 2TP model to fit the NiFe EIS data resulted in a very large disagreement between the experimental points and the model, but the use of the 2TS model gave a very good agreement. Further, Table 5.4 shows that the overpotential behavior of CPE₂ element on the NiFe surfaces is quite opposite to the behavior seen on the other four surfaces *-i.e.* with the increase in overpotential the CPE₂ value decreases. Also, the value of its exponent n_2 on NiFe-1 at low overpotentials is too low to consider the CPE₂ response as an interfacial capacitive response [58]. At the same time Table 5.4 shows that the corresponding resistance R_2 decreases, similarly to the behavior on Ni, NiMo and NiW. In addition, the ratio between the two time constants on NiFe (*i.e.* τ_2/τ_1) is opposite to the one calculated for Ni, NiMo and NiW *-i.e.*

the second time constant, τ_2 , is on NiFe lower than the first time constant, τ_1 , which is related to the HER charge-transfer kinetics. Hence, the response of the HER kinetics is, in the case of the NiFe coatings, recorded in the LF region of the EIS spectra. All these observations, in turn, indicate that the response of the HF time constant, τ_2 , cannot be related to the adsorbed hydrogen. On the other hand, although the use of the 2TS ECC model, that takes into account the impedance response of surface pores, resulted in an excellent agreement between the experimental and simulated data, Table 5.4 shows that the HF time constant, τ_2 , changes with overpotential, which is not consistent with a common behavior related to the response of pores observed in the literature on the HER [23,75,59]. Hence, the HF time constant, τ_2 , on NiFe can neither be related solely to the pure response of the porous structure of the electrode. Current results do not allow us to make a definite conclusion on the physical meaning of the HF time constant, but the overpotential trend of CPE₂, n_2 and R_2 , and their absolute values, indicate that the observed HF response could be related to a response of some fast transfer (most likely charge, rather than mass) processes in the metallic layer very close to the catalyst/electrolyte interface. The presence of a very thin semiconducting oxide film on the NiFe surface, and its response (charge transfer through this film) cannot be either excluded as a possible origin of the observed HF impedance behavior. This might be supported by the fact that the NiFe coatings showed the highest overpotential corresponding to the onset of hydrogen evolution (Figure 5.3) and the lowest transfer coefficient (Table 5.2), which was explained by the presence of a thin oxide film on the electrode surface.

Although EIS and Tafel tehcniques are two quite different experimental techniques (*ac* versus *dc*), results obtained by both of them should be, at least, qualitatively comparable. The Tafel technique gives the dependence of the <u>overall</u> HER rate (measured by current density) on the applied overpotential. Knowing that the HER proceeds in two steps (hydrogen adsorption and subsequent desorption to form molecular hydrogen, Eqs. (2.5) and (2.6)), it is then obvious from the presented EIS analysis that the rate of the HER is related to both the charge transfer R_1 and hydrogen adsorption R_2 resistance (except on NiFe). Hence, combining these two resistances in a series ($R_1 + R_2$) and using the Ohm law it is possible to plot the semi-logarithmic dependence of the HER rate, log ($1/(R_1+R_2)$) versus applied overpotential (Figure 5.7) and compare it to the Tafel plots presented in Figure 5.3. In the case of NiFe, only the

charge-transfer resistance, R_1 , was used to plot the curve, since the resistance R_2 , as previously discussed, is not related to the HER kinetics. It is obvious that the EIS plots in Figure 5.5 follow the trend obtained by *dc* polarization (Figure 5.3). The Ni coating displays the lowest activity, while the NiMo-1 coating again shows the highest activity, followed in a decreasing order of activity by NiMo-2, NiW-1, NiFe1 and NiFe-2. Also, the bimetallic coatings again indicate the presence of two Tafel regions, and the shape of the curves is very similar to the Tafel curves in Figure 5.3.



Figure 5.7 Logarithmic dependence of $1 / (R_1 + R_2)$ on overpotential for the different Ni-Melectrodes.

η	R _{el}	CPE1		R ₁	CPE₁		R ₂	τ.	τ ₂
(V)	(Ω)	$(F s^{n-1} cm^{-2})$	Π ₁	$(\Omega \text{ cm}^2)$	$(F s^{n-1} cm^{-2})$	n_2	$(\Omega \mathrm{cm}^2)$	(s)	(s)
					Ni				
-0.045	2.06	1.66E-04	0.89	6183.1	6.93E-03	1.00	3456.9	5.8E-01	2.4E+01
-0.060	2.11	1.59E-04	0.90	5558.4	1.45E-03	1.00	1529.0	5.2E-01	2.2E+00
-0.085	2.11	1.62E-04	0.90	4588.5	2.05E-03	1.00	1054.3	4.4E-01	2.2E+00
-0.110	2.09	1.62E-04	0.90	3884.5	4.75E-03	1.00	1045.0	3.7E-01	5.0E+00
-0.135	2.09	1.61E-04	0.90	3216.1	3.11E-03	1.00	375.3	3.1E-01	1.2E+00
-0.185	2.08	1.64E-04	0.90	1642.2	1.39E-02	1.00	105.6	1.6E-01	1.5E+00
-0.235	2.09	1.64E-04	0.90	445.6	1.01E-02	1.00	32.0	4.4E-02	3.2E-01
-0.285	2.10	1.52E-04	0.91	126.0	4.34E-03	1.00	15.6	1.2E-02	6.8E-02
-0.335	2.17	1.55E-04	0.91	44.3	1.72E-02	1.00	5.6	4.3E-03	9.6E-02
					NiMo-1				
-0.045	4.04	1.56E-01	0.76	1.601	1.53E-01	0.98	90.02	2.3E-01	1.9E+01
-0.060	3.91	8.07E-02	0.93	0.727	2.71E-01	0.87	23.08	7.0E-02	7.5E+00
-0.085	3.84	8.79E-02	0.94	0.519	3.73E-01	0.85	5.59	5.5E-02	2.4E+00
-0.110	3.7 9	8.92E-02	0.93	0.432	4.84E-01	0.83	2.09	4.5E-02	1.1E+00
-0.135	3.83	1.16E-01	0.90	0.437	4.98E-01	0.95	0.97	5.4E-02	6.4E-01
-0.185	3.83	8.64E-02	0.96	0.312	, 5.96E-01	0.88	0.53	3.4E-02	3.6E-01
-0.235	4.16	8.17E-02	0.99	0.279	5.26E-01	1.00	0.35	3.2E-02	2.6E-01
-0.285	4.03	7.37E-02	0.99	0.234	5.37E-01	1.00	0.27	2.4E-02	2.1E-01
-0.335	3.97	7.92E-02	1.00	0.231	8.70E-01	0.93	0.23	2.7E-02	2.5E-01
	4.02	8.99E-02	0.96	0.249	2.78E+00	1.00	0.11	2.8E-02	4.4E-01
					NiMo-2			· · · · · ·	
-0.045	2.67	5.11E-02	0.92	10.90	4.88E-02	0.95	99.15	6.7E-01	6.9E+00
-0.060	2.67	4.86E-02	0.93	7.62	5.66E-02	0.92	44.32	4.5E-01	3.5E+00
-0.085	2.65	4.95E-02	0.94	4.24	8.11E-02	0.89	11.80	2.6E-01	1.2E+00
-0.110	2.63	5.19E-02	0.94	2.70	1.11E-01	0.87	4.10	1.7E-01	5.5E-01
-0.135	2.61	4.35E-02	0.99	1.54	1.27E-01	0.82	2.19	9.4E-02	2.7E-01
-0.185	2.54	5.73E-02	0.92	1.21	2.67E-01	0.74	0.57	8.0E-02	1.1E-01
-0.235	2.55	5.93E-02	0.91	0.89	3.37E-01	0.66	0.24	5.7E-02	3.6E-02
-0.285	2.55	6.23E-02	0.90	0.78	2.96E-01	0.70	0.19	4.9E-02	2.5E-02
-0.335	2.59	4.58E-02	0.95	0.56	5.26E-01	1.00	0.08	3.1E-02	6.3E-02
<u>-0.435</u>	2.61	7.77E-02	0.83	0.44	-	-	-	2.6E-02	-

Table 5.4 EEC parameters obtained by fitting EIS experimental spectra recorded at various overpotentials on the investigated electrocatalytic coatings using the EEC models presented in Figure 5.6.

Table 5.4 cont.

η	R _{el}	CPE1	0	R ₁	CPE ₁	~	R ₂	T_1	τ_2
(V)	(Ω)	$(F s^{n-1} cm^{-2})$	111	$(\Omega \text{ cm}^2)$	(F s ^{<i>n-1</i>} cm ⁻²)	112	$(\Omega \text{ cm}^2)$	(s)	(s)
					NiW-1				
-0.035	3.25	1.11E-02	0.89	10.76	3.09E-02	0.91	150.97	1.1E-01	6.2E+00
-0.060	2.79	1.41E-02	0.81	10.11	3.57E-02	0.87	36.28	9.1E-02	1.7E+00
-0.085	2.80	1.63E-02	0.80	7.53	5.43E-02	0.87	8.45	7.6E-02	5.6E-01
-0.110	2.54	1.83E-02	0.78	5.73	8.76E-02	0.91	2.26	5.9E-02	2.5E-01
-0.135	2.69	1.89E-02	0.80	4.16	1.95E-01	0.92	0.68	4.9E-02	1.6E-01
-0.185	2.56	2.19E-02	0.78	2.58	-	-	-	3.1E-02	-
-0.235	2.44	2.15E-02	0.78	1.65	-	-	-	1.9E-02	-
-0.285	2.47	2.03E-02	0.80	1.18	-	-	-	1.3E-02	-
-0.335	2.41	2.59E-02	0.75	0.91	-	-	-	9.7E-03	-
0.435	2.44	3.13E-02	0.73	0.59	-	-	-	6.2E-03	-
					NiFe-1			_	
-0.150	0.89	1.31E-03	0.92	162.01	4.73E-02	0.22	9.47	1.7E-01	1.1E-01
-0.160	1.13	1.29E-03	0.92	136.00	3.59E-02	0.25	7.09	1.4E-01	1.6E-02
-0.185	1.46	1.26E-03	0.92	85.08	2.73E-02	0.29	6.02	8.8E-02	5.9E-03
-0.210	1.75	1.29E-03	0.91	50.28	1.75E-02	0.35	5.01	5.2E-02	2.1E-03
-0.235	1.90	1.38E-03	0.90	30.04	1.26E-02	0.38	4.27	3.0E-02	1.0E-03
-0.285	2.06	1.72E-03	0.86	12.16	6.23E-03	0.46	0.32	1.2E-02	2.6E-06
-0.335	2.14	2.38E-03	0.81	5.57	3.34E-03	0.51	2.47	5.4E-03	1.2E-04
-0.385	2.26	3.38E-03	0.76	2.87	1.88E-03	0.57	1.93	2.7E-03	6.6E-05
-0.435	2.51	4.73E-03	0.66	2.19	2.89E-04	0.77	1.03	1.1E-03	3.9E-05
					NiFe-2				
-0.225	2.25	8.77E-04	0.94	44.83	8.48E-03	0.59	6.30	3.8E-02	1.2E-02
-0.230	2.21	1.18E-03	0.90	32.38	1.07E-02	0.56	4.91	2.8E-02	8.9E-03
-0.235	2.20	1.13E-03	0.87	29.33	1.37E-02	0.54	2.97	2.0E-02	4.7E-03
-0.260	2.22	1.32E-03	0.82	20.63	1.17E-02	0.57	1.02	1.0E-02	7.6E-04
-0.285	2.26	1.66E-03	0.77	14.70	6.34E-03	0.65	0.45	6.4E-03	2.2E-04
-0.310	2.27	1.95E-03	0.74	10.90	2.63E-03	0.76	0.24	4.2E-03	9.8E-05
-0.335	2.28	2.10E-03	0.72	8.26	8.81E-04	0.89	0.14	2.9E-03	6.1E-05
-0.385	2.36	2.30E-03	0.70	4.88	9.78E-04	1.00	0.06	1.5E-03	7.9E-05
-0.435	2.34	2.94E-03	0.66	3.02	4.08E-03	1.00	0.17	8.3E-04	9.8E-04
-0.535	2.29	2.04E-03	0.70	1.57	-	-	-	3.3E-04	-
-0.635	2.30	1.78E-03	0.70	0.97	-	-	-	1.6E-04	-

5.1.5 Intrinsic electrocatalytic activity

Besides the information on the kinetics of the HER, EIS results can also be used to estimate the real surface area of the coatings. This is important because, by knowing the real electrochemically active area of the catalyst, it is possible to conclude on the intrinsic activity of the material in the HER, by subtracting for the surface-area effect. As already mentioned before, there are several techniques that can be used to determine a true surface area of a catalyst, but the EIS technique was proposed [21,22,24,69,70] as the most appropriate technique that can be used for the true surface area determination in electrochemical systems. Using this technique, the real surface area can be estimated form the double layer capacitance. Thus, this is the true, electrochemically accessible surface area on which the hydrogen can adsorb, and it is usually larger than the geometrical area of the catalyst surface. Taking into account that the average of the double layer capacitance of a smooth metal surface is 20 µFcm⁻² [71,87], the real area can be calculated as $A_{real} = C_{DL}/20$ (cm²), and then the roughness factor, that characterizes the ratio of the real to the geometrical surface area, can be calculated as $\sigma = A_{rea}/A_{geometric}$. As previously defined, the double layer capacitance is described by the constant phase element CPE₁ and its exponent n_1 . However, although the value of parameter n_1 is close to unity, its small deviation indicates the presence of surface inhomogenities, most likely in terms of the charge distribution, rather than in terms of the surface roughness, and the actual value of the double layer capacitance, C_{DL} , can then be calculated using the equation originally proposed by Brug et al. [88] and latter used by many researchers [15,24,77]:

$$C_{DL} = \left[\frac{CPE}{(R_{el}^{-1} + R_1)^{(1-n)}}\right]^{1_n}$$
(5.5)

The mean values of the double layer capacitance, the true surface area and the roughness factor are presented in Table 5.5.

catalyst	C _{DL} (F)	A _{real} (cm ²)	σ
Ni	$(4.4 \pm 0.2) \times 10^{-5}$	2.2	3.2
NiMo-1	$(5.2 \pm 0.5) \times 10^{-2}$	2608	3779
NiMo-2	$(2.8 \pm 0.2) \times 10^{-2}$	1416	2052
NiW-1	$(4.6 \pm 0.4) \times 10^{-3}$	232	336
NiFe-1	$(4.8\pm0.1)\times10^{-5}$	21	35
NiFe-2	$(3.3 \pm 0.8) \times 10^{-5}$	16	24

Table 5.5 Double layer capacitance, real surface area and corresponding surface roughness values for the investigated catalytic coatings calculated from the EIS data.

Table 5.5 shows that the double layer capacitance standard deviation is rather small *-i.e.* the value of the double layer capacitance does not change significantly with overpotential, which indicates that the accessibility of the catalyst surface to the electrolyte remains constant. Only in the case of the NiFe coatings the double layer capacitance gradually decreased, indicating the blockage of the surface most likely by adsorbed hydrogen. Hence, the calculation of the real surface area of the NiFe coatings was based on the capacitance values obtained at low overpotentials. The constant value of the double layer capacitance on Ni, NiMo and NiW also confirmed that the change in the Tafel slope in Figure 5.3 is not a result of a decreased surface area, but the formation of hydrides, which was already discussed.

Obviously, in order to design a good electrocatalyst, one of the major goals it to achieve a large true surface area per geometric area ratio *-i.e.* the roughness factor. As it can be seen from Table 5.5, pure Ni is the catalyst with the lowest roughness factor value, while NiMo-1 is the catalyst with the highest roughness. This result is in accordance with the SEM images (Figure 5.2). Similar values of the surface roughness for Ni were also obtained for polished polycrystalline Ni electrodes [13,21,22] and electrodeposited Ni coatings [89], while for bimetallic and Raney-type alloys much higher values were obtained; 300 for NiZr [21], 1000 for NiZn [87], 2800 for NiFe [24], 5500 for NiZnP [22] and 7000 for NiAI [15]. Considering that the high surface area electrodes for the HER are usually obtained by a chemical treatment of the electrode *-i.e.* by leaching a more active component out of the alloy (*e.g.* Zn from a NiZn alloy), and comparing the surface roughness of the NiMo-1 coating to the values obtained on the Raney-type electrodes outlined above- it could be said that the very simple (still unoptimized) electrodeposition method used here gave very comparable results to the more complex

method for the production of Raney-type electrodes. However, the surface roughness obtained on the other four electrodes is lower than on NiMo-1 (Table 5.5), which could be partially due to the difference in the intrinsic mechanism of nucleation and growth of the coating, and partially due to the fact that the used electrodeposition procedure was not optimized in order to obtain a highest possible surface roughness for a given surface composition.

Now, knowing the real electrochemically accessible area of the studied coatings, it is easy to compare their intrinsic catalytic activity. For this purpose the Tafel plots presented in Figure 5.3 were normalized to the true surface area dividing the current by the roughness factor. Table 5.6 lists the values of the exchange current density and the current recorded at overpotential -150 mV for the electrocatalys used in research. Due to the large overpotential for the onset of the HER on NiFe-2, it was not possible to determine the HER current at -150 mV.

Table 5.6 Exchange current density and current density at overpotential of -150 m
obtained from Tafel plots (Figure 5.3), normalized to the true surface area of the catalyst
The most right column represents the inverse of the kinetic resistance normalized to the
true surface area of the electrode obtained from Figure 5.7.

		Tafel	EIS	
catalyst	j₀/σ	<i>j</i> / σ at -150 mV	10 ⁵ /(<i>R</i> ₁+ <i>R</i> ₂)σ at -150 mV	
	(µA cm ⁻²)	(μA cm ⁻²)	(Ω ⁻¹ cm ⁻²)	
Ni	-0.797	-8.4	10.0	
NiMo-1	-0.005	-14.9	22.4	
NiMo-2	-0.006	-11.2	17.5	
NiW-1	-0.031	-31.1	78.1	
NiFe-1	-0.056	-1.8	18.5	
NiFe-2	-0.015	-		

In terms of the exchange current density, Table 5.6 shows that the pure Ni coating yields the highest intrinsic electrocatalytic activity at the HER equilibrium potential. However, since the HER reaction does not occur at the thermodynamic potential (zero overpotential), but certain overpotential is required, the comparison of exchange current density values cannot be used as the only criteria for the comparison of catalytic activity. It has been reported that a value of the Tafel slope (*i.e.* the high value of transfer coefficient) in the low overpotential region is as, or even more, important than favorable exchange current density [24]. This is clearly illustrated in Table 3.6 which
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also lists the current density at overpotential -150 mV. In this case, which actually simulates the working situation in a hydrogen generator, NiW-1 appears to yield the highest electrocatalytic activity, followed by NiMo-1, NiMo-2, Ni and NiFe-1. Similar trend was also obtained from EIS measurements (Table 5.6), where the NiW-1 coating showed the best electrocatalytic activity, while Ni yields the lowest electrocatalytic activity. The trend listed in Table 5.6 is different than the one shown in Table 5.3, where the corresponding current density values were normalized to the geometric area, and NiMo-1 showed to be the *overall* best catalyst. However, since the production of hydrogen in a real hydrogen generator is related to the *overall* current, one can conclude that NiMo-1 indeed represents the best investigated catalytic coating. On the other hand, by optimizing the conditions for the electrodeposition of NiW in terms of achieving the surface roughness equal or even larger than on NiMo-1, the NiW catalyst would, in principle, offer the best choice among the investigated materials.

One interesting observation that can be noticed form Table 5.6 is that, with an exception of NiFe, bicomponent coatings NiMo-1, NiMo-2 and NiW-1 offer a higher intrinsic activity when compared to polycrystalline Ni. It is well known that the HER electrocatalytic activity of Ni can be improved by the addition of a second metal into the alloy. A general conclusion is that the intrinsic catalytic activity for the HER is related to the electronic structure of metals, although any explicit and comprehensive explanation has not yet been given. The theoretical approach to explain the HER activity of alloy catalysts is even more complex, and several theories have been proposed. The alloying effect of transition metal-based alloys on both hydrogen evolution activity and catalyst stability has been discussed by Jaksic et al. [90,91] on the basis of the Engel-Brewer valence-bond theory, as a generalized Lewis acid-base reaction model. This research group postulates that the intermetallic and interionic combination of elements on the left hand side of transition series -that have empty or half filled d-orbital (hypo-d-electronic elements, e.g. Mo, W, V, etc.)- with metals of the right half of the transition series -having internally paired d-electrons (hyper-d-electronic elements, e.g. Ni, Pd, Pt, Co, etc.), otherwise not available for bonding in the pure metal-, results in a significant change of their bonding strength and, consequently, increased intermetallic stability, whose maximum usually coincides with optimal d⁸-electrons for the synergism and maximal activity in the HER. In such hypo-hyper-d-electronic interactions paired d-electrons of the hyper-d-electronic element, undergo partial or total delocalization and transfer to the halffilled or empty semi-*d*-shells of the hypo-*d*-electronic element. They postulate that intermetallic and interionic combinations of above elements yield a HER volcano plot behavior, with a maximum corresponding to symmetric Laves phase (*e.g.* NiMo₃, PtMo₃, PtW₃, CoMo₃, *etc.*). The *d*-band has been claimed to be crucial in (electro)catalytic hydrogen reactions (it represents both bonding and adsorptive band), while the overall kinetics of the HER has been, on the other hand, related to the electronic density. The theory proposed by this research group has been supported by a number of experimental studies related to the direction of electron transfer, postulated by Jaksic, can also be found in recent papers published by Wieckowski *et al.* [93-95], where it has been shown, using NMR and XPS, that alloying Pt with Ru results in the decrease in total density of states at the Fermi level of Pt atoms *-i.e.* the direction of electron transfer is from Pt to Ru.

Another theory related to the synergism of HER bimetallic catalysts has been proposed by Ezaki et al. [18-20]. They also based their explanation on the electronic structures of alloys. However, the main difference between the two theories is in the direction of electron transfer between constituting atoms in the alloy and its effect on the respective Fermi levels of the components. The latter theory explains the variation in hydrogen overpotential (*i.e.* HER electrocatalytic activity) in terms of the direction of the charge transfer between atoms in a transition metal based binary alloys. Experimental results have been explained using the DV-X α cluster method. Namely, if the alloying element is more electronegative than the base metal, the charge transfer occurs from the base metal to the alloying element. In that case, excess electrons are located near the alloying metal, which then provides preferable sites for hydrogen evolution reactions, since the excess electrons promote proton discharge. Consequently, the corresponding hydrogen overpotential of the alloy reveals the value characteristic of the alloying metal rather than the base metal. Contrary to this, if the alloying metal is less electronegative than the base metal, the transfer of charge occurs from the alloying metal to the base metal, and, therefore, the base metal behaves as the active site for hydrogen evolution. Consequently, the hydrogen overpotential of the alloy is similar to that of the base metal and less dependent on the alloying metal. This group also postulates that the Fermi energy level seems to be in correlation with the hydrogen overpotential of alloys when the alloying element is more electronegative than the base metal. Although this theory

disagrees with Jaksic's theory in terms of the direction of electron transfer, it also has an experimental support in works of Oelhafen et al. [96-98]. Namely, the UPS spectra recorded on Ni-Zr showed that the high binding energy peak in the UPS spectra is related to the 3d Ni states and the peak near the Fermi energy to the 4d Zr states. When compared to pure metals, the shift of the 3d Ni band to higher binding energies results in a decrease of the local density of states at the Fermi level for Ni. The transfer of electrons from the 4d-band of the less electronegative Zr to the 3d-band of the more electronegative Ni explains this shift. Applying this conclusion on the bimetallic coatings presented here, it would mean that in the NiMo-1, NiMo-2, NiW, NiFe-1 and NiFe-2 coatings the higher electron density would be around Ni-sites and, therefore, Ni would act as a source of electron supply to the proton. Hence, the HER would occur near the Ni sites, which is also postulated by Ezaki et al. [18-20]. This group also predicts that the increase in the HER electrocatalytic activity coincides with the increase in electron density around the more electronegative constituent of an alloy, which would mean that one of the best HER catalyst would be NiTi. Our results indeed show that the increase in the HER electrocatalytic activity coincides with the increase in the electron density around Ni-sites, but at the same time the results presented cannot give a general conclusion on the trend. On the other side, Jaksic's theory predicts an optimum electron density for the best HER electrocatalytic activity of an alloy, and does not recognize specific surface sites (in terms of alloy constituents) as a hydrogen active sites. Similar conclusions have been reported by Kawashima et al. [55]. They have shown that the optimum electron configuration corresponds to the situation of a nearly filled d orbital. The *d*-band vacancy of Ni in NiMo and NiW alloys decreases with the addition of Mo or W and becomes nearly zero at ca. 11 at.% Mo and 8 at.% W. These two compositions would, hence, give the best activity towards the HER, which is in good agreement with their results, and results obtained on NiMo metal ultra-fine particles [25]. Our results on NiMo also support the assumption that the highest activity in the HER can be expected at the composition 11 at.% Mo. Comparing the activity of NiMo-1, NiMo-2 and Ni surfaces at -150 mV (Table 5.6), it can be seen that the most active among them is exactly the one that gives the optimum electron density for the HER -i.e. NiMo-1 (12 at.% of Mo). However, the results presented in the table show that NiW-1 coating offers even better HER catalytic activity than NiMo-1, although the content of W in the coating is 23 at.% -*i.e.* almost three times higher than the optimum content (8 at.%). The exact reason for this deviation in the predicted behavior is not obvious from the presented results,

neither the reason for a higher electrocatalytic activity of NiW-1 compared to NiMo-1, which is opposite to the behavior reported in [55]. One of the possible explanations for the latter could be related to the crystalline structure of coatings, Figure 5.1. NiMo-1 coating is amorphous, while NiW-1 coating is crystalline, and it has already been shown that crystalline materials are more active towards the HER than amorphous [61,99], which is due to the larger number of electrochemically active sites on the surface. While the previous two theories and explanations take into account solely the influence of electronic density (distribution) on the corresponding electrocatalytic HER activity, the well-known 'spillover' process in heterogeneous catalysis has also been used to interpret the synergism of transition metal based HER alloys, more specifically NiMo [17]. In this theory simple cooperative functioning of the components is mediated via rapid intra- and inter-particle surface diffusion of H ad-atoms. The authors postulate that Ni sites on the NiMo surface influence proton discharge and serve as a hydrogen source for neighboring Mo sites which act as hydrogen 'trap' sites where ion/atom recombination, and molecular hydrogen desortption is promoted more efficiently. The authors of [17] essentially rule out any relationship between the electronic interactions among the NiMo alloys components and observed synergy. However, the opinion of our research group is that the influence of the electronic structure on the catalytic activity of bimetallic catalysts plays one of the major roles in the kinetics of the HER, but the surface diffusion cannot be completely excluded as a contributing factor. This opinion is logical if we consider the HER reaction mechanism, Eqs.(2.5-2.7), from which is obvious that the kinetics of the HER depends on both the electron-transfer rate and the strength of the M-H_{ads} bond, which both, in turn, depend on the *d*-electron density at the Fermi level. This opinion is supported by the experimental results of Wieckowski et al. [93,95], who have recently shown that alloying Pt with Ru induces major changes in the core-level binding energies of chemisorbed carbon monoxide (CO). Schlapka et al. [100] have also recently shown that the electronic effect plays the major role on the adsorption strength of CO on up to four monolayers of Pt on Ru, after which a surface strain effect starts to predominate.

From the results presented in this thesis and subsequent discussion it is evident that all three major theories could be used to explain the increase in the HER activity upon alloying Ni with W and Mo (Table 5.6). Some concepts of the theories are mutually contradictory, and the author's opinion is that none of them gives general definite explanations of the source of synergy observed in bicomponent HER catalysts. However, the author and the research group agree with the fact that the improvement in the HER electrocatalytic activity is related to the electron density distribution, and thus, that the design of HER electrocatalysts starts at an 'electronic level'. However, the direct relationship between the electron density distribution and HER electrocatalytic activity is not always observed and some additional effects, such as the surface diffusion [17] or strain effect should also be considered [101]. This requires further thorough and systematic investigation of the influence of all these effects on the materials' electrocatalytic activity in the HER, which is a subject of the present and future research in the supervisor's laboratory.

5.2 Ni / CP / GC catalysts

5.2.1 Morphology of the electrodes

As previously mentioned, the aim of using conducting polymers PPY and PANI was use them as 'pattering matrices' in order to increase the surface area of HER catalyst Ni, and hence to produce more active sites available for the HER. Therefore, the morphology of the conducting polymer coatings deposited on the GC substrate should be known. In order to examine the morphology of the polymer matrices used to electrodeposit nickel, scanning electron microscopy (SEM) was used. The SEM images in Figure 5.8 show significant differences in morphology between the two polymers.



Figure 5.8 SEM images showing the surface morphology of (a) Polypyrrole and (b) Polyaniline electrodeposited on a GC substrate.

The PPY matrix (Figure 5.8a) shows a compact homogeneous surface with micro-pores. These micro-pores provide a path for nickel to the GC substrate for its electrochemical deposition and growth, thus making the PPY matrix potentially better for the nickel electrodeposition than a flat metal substrate. On the other hand, from Figure 5.8b it can be observed that the PANI matrix offers a completely different morphology. The matrix has a highly fibrilar and porous structure, which indicates that it could offer better pattering properties than the PPY matrix. This turns to be true, as it will be shown later.

The micrographs of the different Ni / CP / GC catalysts are presented in Figure 5.9. The SEM images show significant differences in morphology between the

investigated catalytic coatings. The Ni / PPY electrode (Figure 5.9a) shows Ni islands distributed evenly throughout the surface. The islands size distribution is rather wide, ranging from ca. 100 nm to 3 μm. Similar studies [102,103] have suggested that the metal particles are formed by initial nucleation at the polymer/carbon interface inside the micro-pores, followed by growth through the polymer film. Since PPY (and PANI) are not electrically conductive in the region of Ni electrodeposition (-1.45 V vs. MSE), there is no possibility for Ni to nucleate and grow on top of the PPY matrix, or inside the matrix. The nucleation starts at the GC / PPY-pore-electrolyte interface, and the growth continues through the pores of the PPY matrix towards the outer PPY/electrolyte interface (Figure 5.10a). This also could suggest that Ni particles might be deposited at different depths into the polymer -i.e. some protrude out of the surface, like in the SEM image, while some might stay 'burried' inside the PPY matrix.



(a)

(b)



(c)

Figure 5.9 SEM images showing the surface morphology of (a) Ni / PPY, (b) Ni / PPY – Co and (c) Ni / PANI electrodes.





Considering that the nucleation and growth of Ni starts at the GC PPY-free surface, and analyzing the SEM image (Figure 5.9a), it can be assumed that the nickel deposited on/inside the PPY film matrix have a mushroom type of morphology, where the top of the mushroom is emerging outside the polymer and the stem is inside the polymer film, down to the GC surface (Figure 5.10a).

A significant difference can be observed between the SEM images of the two types of Ni / PPY catalysts. In Figure 5.9b the micrograph of the Ni / PPY co-deposited coating shows much smaller Ni islands (diameter between ca. 100 and 300 nm) evenly distributed throughout the entire surface (some small agglomeration of islands is noticable). In addition, a higher particle density can be observed. This can be attributed to a higher polymer porosity achieved during co-deposition. The co-deposition procedure consists in cycling the electrode between the deposition potentials of PPY and Ni for a certain number of cycles, as explained in section 4.3.2.2. In the first cycle, a thin highly porous layer of polymer is deposited on the GC substrate. Immediately after the first polymer film is formed, nickel deposits on the GC surface through a highly porous structure of the thin PPY layer. This prevents polymer pore blockage in the subsequent PPY deposition cycles because the pores are already filled with nickel metal particles. The polymer film keeps growing on the already deposited polymer and nickel on the already deposited nickel particles (Figure 5.10b). On the contrary, when the PPY matrix is formed at a constant potential, before the Ni electrodeposition, its porosity depends on the PPY matrix thickness, as it is going to be explained in the following section.

The micrograph of a Ni / PANI coating, Figure 5.8c, differs significantly from the previous two coatings. The latter showed a two-dimensional layer of Ni islands on top of the PPY matrix, connected with the GC surface through PPY pores through which nickel grew. On the other hand, the micrograph of a Ni / PANI coating shows that the electrode is covered by a three-dimensional layer of globular nickel particles of an average diameter 4 µm. The particles seem to be growing from the GC substrate over the PANI fibrils in a three-dimension arrangement. Assuming that the Ni globular particles are electrically interconnected, one can easily conclude that the surface are available for the HER reaction on a Ni / PANI coating is the highest among the investigated Ni / CP coatings, and higher than the Ni coating deposited on a Cu substrate (Figure 5.2). This was proved by dc and ac measurements, which will be discussed later in the text. The micrographs presented in this section indicate that the chemistry, surface charge distribution and morphology of a CP matrix play the major role that governs the subsequent morphology of the Ni islands/particles on the electrode surface. Hence, by fine-tuning chemical (electrolyte) and deposition (potential / current) conditions during the (co)deposition of PPY, PANi, and Ni, it is possible to achieve even larger porosity of the CP matrices, and thus, further increase the surface area of electrodeposited Ni electrocatalyts.

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5.2.2 Linear Tafel polarization

As it was mentioned before, the porous structure and high surface area of conducting polymers is attractive for their use as supporting material for the development of new catalysts for the HER. The purpose of using CPs is to pattern a GC substrate surface in a way to achieve controlled growth of a catalyst layer, and to also extend the catalyst layer into the electrolyte, making it three-dimensional. Hence, the CP matrix also serves as a 'skeleton' for the growth of a catalyst layer. Polypyrrole (PPY) and polyaniline (PANI) were used as matrices to electrodeposit nickel on a GC electrode substrate, and in the previous section, the morphology of the resulting catalytic layers was discussed. In this section, results on the HER electrocatalytic activity of the Ni / CP / GC catalysts are discussed on the basis of recorded Tafel polarization curves. The influence of a CP deposition time, Ni deposition time, and number of cycles in the co-deposition procedure on the resulting catalytic activity was investigated.

Figures 5.11 and 5.12 show the polarization curves for hydrogen evolution in $0.5M H_2SO_4$ at two PPY and Ni deposition times, respectively. The co-deposition mode was used only in the case of Ni / PPY (Figure 5.13), while an attempt to do the co-deposition of Ni and PANI did not result in any nickel deposited in the polymer matrix nor on its surface. The reason for this is not known and requires further investigation and co-deposition optimization.

From Figure 5.11, it can be observed that for a fixed Ni deposition time (20 min), the Tafel polarization curve of the catalyst with a shorter PPY deposition time (2.5 min) yields higher HER current densities than the curve of the catalyst with a longer PPY deposition time (5 min). Hence, the catalyst layer formed at a shorter PPY deposition time offers a higher catalytic activity for the HER. This variation in catalytic activity for the two PPY deposition times is bigger at longer nickel deposition times (Figure 5.14).



Figure 5.11 Linear Tafel polarization curves for a fixed Ni deposition time (20 min) and different PPY deposition times (2.5 and 5 min).



Figure 5.12 Linear Tafel polarization curves for a fixed PPY deposition time (2.5 min) and different Ni deposition times (20 min and 1 h 40 min).

On the other hand, Figure 5.12 shows the Tafel curves for a fixed PPY deposition time (2.5 min) and two different Ni deposition times. It can be observed that the curve of the catalyst with a longer Ni deposition time (1 h 40 min) gives higher current densities than the curve with shorter Ni deposition time (20 min), indicating that the catalyst with longer nickel deposition time is a better catalyst. The variation in catalytic activity for the two different Ni deposition times is less at longer PPY deposition times (see Figure 5.14).

These results can be explained by understanding the morphological structure of the polymer and the metal deposition mechanism. Polypyrrole has a compact microporous structure. The micro-pores provide a path for nickel to reach the GC surface, nucleate on it and grow back towards the outer PPY/electrolyte interface. At short PPY deposition times, the polymer layer is thin and a large number of pores are available for nickel deposition. However, at long PPY deposition times, the polymer layer becomes thicker and pores get terminated by the same growing structure of the polymer, leaving fewer free paths to the GC surface for nickel deposition. Therefore, lower PPY deposition times are better for the subsequent catalyst deposition. Similar studies [9,48] have suggested that the metal particles are formed by initial nucleation at the polymer/carbon interface, followed by growth through the pores of the polymer. Thus, longer nickel deposition times lead to an increase in the nickel loading, and most likely result in spreading of the Ni 'islands' at the outer PPY/electrolyte interface, thus offering an increase in the total catalyst area available for the HER.

In the case of Ni / PPY co-deposition, Figure 5.13 shows that the curve with a larger number of cycles (40 cycles) reveals a higher catalytical activity for the HER. This can be explained on the basis of a co-deposition mechanism. During co-deposition, a first thin layer of polymer is deposited on the GC substrate for 5 seconds. Since this first layer is very thin it is highly porous. Immediately after the first layer of PPY film is formed, the deposition of nickel on a GC surface occurs through a large number of pores (paths) for 2 seconds, resulting in the formation of a large number of Ni islands 'embedded' into the first PPY layer. This prevents the PPY pore blockage in the subsequent cycles since the pores are already filled with nickel. The polymer film keeps growing on the already (pre)deposited polymer and nickel on the already (pre)deposited nickel particles. Consequently, one can assume that by increasing the number of cycles this 3D layer can



grow thicker, thus resulting in a higher catalytical activity for the HER due to the increased surface area of the catalyst. This is clearly observed in Figure 5.13.

Figure 5.13 Linear Tafel polarization curves for Ni / PPY co-deposited coatings produced by polarizing the electrode for 20 and 40 cycles.

Figure 5.14 summarizes all the Tafel results obtained using the Ni / PPY electrodes. The best electrocatalytic performance is offered by the Ni / PPY - 1:40 / 2.5 electrode -i.e. combining the short PPY deposition time and long Ni deposition time. Quite opposite results are obtained when the long PPY deposition time is used (5 min) and short Ni deposition time (20 min) -i.e. when the Ni / PPY – 20 / 5 electrode is used. The electrodes made by co-deposition offer intermediate performances. However, the Ni / PPY – Co – 40 electrode could be further optimized in order to increase the Ni-surface area (e.g. by increasing the number of co-deposition cycles), which most likely cannot be done with the Ni / PPY – 1:40 / 2.5 electrode by increasing the time of Ni deposition. This could, actually, result in a decrease in the Ni active surface area due to the formation of a compact Ni layer on top of the PPY layer, by merger of Ni islands at longer deposition times. Nevertheless, this is a point that requires further investigation and was out of the scope of the present thesis.



Figure 5.14 Linear Tafel polarization curves of all the different cases studied (influence of PPY deposition time, Ni deposition time, and number of cycles in the co-deposition procedure) on the Ni / PPY electrocatalysts.

The same deposition times used for PPY were also investigated using PANI. However, different results can be observed. Significantly higher catalytical activity was obtained when PANI deposition time was 5 min and not 2.5 min (Figure 5.15). This is due to the morphological structure of PANI. Polyaniline has a fibrillar structure, with high surface area, considerably higher porosity and lower diffusion resistance than PPY. Furthermore, longer polymer deposition times give thicker PANI layers with higher surface area for the nickel deposition.



Figure 5.15 Linear Tafel polarization curves for a fixed Ni deposition time (20 min) and different PANI deposition times (2.5 and 5 min).



Figure 5.16 Linear Tafel polarization curves for a fixed PANI deposition time (5 min) and different Ni deposition times (20 min and 1 h 40 min).

Also contrary to the results on PPY (Figure 5.12), Figure 5.16 shows that for a fixed 5 min PANI deposition, the catalyst layer formed at a longer Ni deposition time (1 hr 40 min) offers inferior catalytic activity compared to the catalyst formed at a shorter Ni deposition time (20 min), while for a fixed 2.5 min PANI deposition time, the opposite can be observed (Figure 5.17). This occurs because at short PANI deposition times, the polymer layer is thinner and longer nickel deposition favors a high metal loading, with a catalyst layer that can grow past the outer PANI/electrolyte interface. On the other hand, at long PANI deposition times, the polymer layer is the polymer layer is the polymer layer by the growing nickel particles, thus diminishing the total surface area of nickel available for the HER.



Figure 5.17 Linear Tafel polarization curves for a fixed PANI deposition time (2.5 min) and different Ni deposition times (20 min and 1 h 40 min).



Figure 5.18 Linear Tafel polarization curves of the all the different cases studied (influence of PANI deposition time and Ni deposition time) on the Ni / PANI electrocatalysts.

The previous figures show individual cases separately, but in order to relatively compare the Ni / PANI catalysts Figure 5.18 was plotted. It appears that the Ni / PANI – 20 / 5 catalyst offer the overall best catalytic activity among the Ni/PANI catalysts investigation, while the worst electrocatalytic activity was obtained using the Ni / PANI – 20 / 2.5 catalyst. The other two catalysts are grouped closer to the best Ni / PANI catalyst, and their polarization curves overlap. This demonstrates that if Ni is deposited for a longer time (1 h 40 min), the PANI deposition time (i.e. the thickness of a PANI matrix layer) does not have any influence on the resulting HER electrocatalytic activity. This, in turns, indicates that at longer Ni deposition times a partial blocking of the inner Ni layer (a layer inside the PANI matrix 3D structure) occurs, thus diminishing the Ni surface area available for the reaction.

In order to compare the relative electrocatalytic activity of the Ni / CP coatings that gave the highest electrocatalytic activity within the group, the Tafel curves recorded

on the best-group catalysts have been plotted on the same Tafel graph (Figure 5.19.), together with a Tafel curve of pure nickel on a Cu substrate as a control. This plot now offers a clear picture on the performance of all the 'best' HER Ni / CP catalysts.



Figure 5.19 Linear Tafel polarization curves of the best Ni / CP electrocatalysts in comparison to the Ni electrocatalyst electrodeposited on a Cu substrate (Ni/Cu).

From Figure 5.19 it can be observed that all the Tafel curves are similar in terms of the Tafel slope (Table 5.7). There is no evidence on the change of the reaction mechanism with the increase in overpotential, as in the case of bimetallic coatings deposited on Cu (Figure 5.3). At very high overpotentials the curves recorded on the PPY-based catalysts deviate from the linearity, towards lower current densities. Possible origins of such behavior have been discussed previously (section 5.1.3). However, the two most probable reasons for the deviation are related to the (*i*) blockage of a catalyst's surface due to the extensive hydrogen evolution; and (*ii*) possible presence of mass-transport limitations occurring along the NI / PPY interface boundary. The blockage is expected to be located at the PPY / Ni interface boundary, within the polymer matrix. In support of this conclusion is the Tafel curve recorded on the Ni / PANI catalyst, which does not show any deviation in the slope at the extreme overpotentials. This is reasonable to expect if we refer to the SEM image of the Ni / PANI coating (Figure 5.9c),

which shows a large porosity of the catalyst layer, thus ensuring that the build up of produced hydrogen does not occur in the overpotential window investigated. In the case of mass-transport limitations along the NI / PPY interface boundary, which occur due to the partial physical obstruction of the mass transport between the Ni and PPY towards the interior of the catalyst layer, the increase in electron transfer rate (by the overpotential increase) would result in the dominance of the mass transport effect. This would, in turn, give a 'diffusion-limited' Tafel curve shape. The beginning of this "diffusion-limited-like' region can actually be observed in Figure 5.19 on the Ni / PPY catalysts. However, this possibility can be dismissed as a possible reason for the observed deviation in the Tafel slope, since the EIS measurements did not show any presence of mass-transport limitations (Table 5.9.). Hence, the extensive accumulation of molecular hydrogen between the Ni and PPY layers (i.e. at the interface boundary), which occurs at extreme overpotentials, is the reason for the observed deviation. This information is important since it indicates that the change in the structure of the Ni / PPY interface boundary could significantly influence the kinetics of the HER at high overpotentials. This could be achieved by optimizing the conditions of the PPY and/or Ni deposition, or by changing the morphology of the PPY layer using chemical routes (e.g. partial or complete dissolution, introduction of chemicals that cause pot-deposition stiffening of the layer, etc.).

The values of the Tafel slope obtained from the curves in Figure 5.19 are presented in Table 5.7, together with the corresponding exchange current density and transfer coefficient values. Considering the HER reaction mechanism (Eqs. (2.5-2.7)) and its corresponding Tafel slope values (120 / 40 / 30 mV decade⁻¹, respectively), it is clear that the values presented in the table show that the *rds* on the Ni / CP coatings is the Volmer reaction step *-i.e.* the adsorption of a proton. This is in accordance with the HER reaction mechanism observed on nickel deposited on Cu. However, comparing the transfer coefficients between the Ni / CP catalysts and the Ni / Cu catalyst (Table 5.7), it seems that all the Ni / CP catalysts offer slightly better electrocatalytic activity in terms of the invested energy used. The exchange current density values demonstrate a superior electrocatalytic activity of the Ni / CP catalysts at the equilibrium HER potential (zero overpotential), relative to the Ni / Cu catalyst. The Ni / PANI – 20 / 5 catalyst offers the highest activity, almost 20 times higher than the Ni / Cu catalyst.

Catalyst	<i>b</i> (mV decade ⁻¹)	<i>j₀</i> (µA cm ⁻²)_	α
Ni / Cu	147	-2.6	0.39
Ni / PANI – 20 / 5	133	-47.3	0.44
Ni / PPY – 1:40 / 2.5	40	-45.9	0.44
Ni / PPY – Co – 40	43	-25.7	0.43

Table 5.7 HER kinetic parameters obtained by the analysis of the Tafel curves presented in Figure 5.19.

Even though Ni / PANI – 5 / 20 and Ni / PPY – 2.5 / 1:40 have a very close value of exchange current density, the former is considered a better catalyst because it has a better catalytic activity at higher overpotentials.

However, since the actual hydrogen generator does not work at equilibrium conditions, a certain overpotential is required in order to produce hydrogen. A very common way of comparing the HER electrocatalysts is to evaluate their activities at a certain applied overpotential or certain fixed current density (hydrogen production rate), as already discussed in Section 5.1.3. The values of overpotentials for each catalyst at fixed current density (i.e. hydrogen "production" rate) of 1 mA cm⁻² are presented in Table 5.8. This gives an indication of the amount of energy (overpotential) that has to be invested to produce a fixed amount of hydrogen.

Table 5.8 Comparison of the electrocatalytic activity of the investigated Ni / CP / GC catalyst coatings in terms of (*a*) the overpotential and power input needed for a fixed hydrogen production rate determined by the current density of 1 mA cm⁻², and of (*b*) the resulted production rate at a fixed energy input (fixed overpotential of -150 mV).

Catalyst	<i>j</i> = 1 n	$nA cm^{-2}$	η = -150 mV		
	η	Power	j	Volume of H ₂	
	(mV)	<u>(mvv)</u>	(mA cm ⁻)	<u> (Lh') </u>	
Ni / Cu	-379	0.379	-0.027	6	
Ni / PANI – 20 / 5	-175	0.175	-0.647	145	
Ni / PPY – 1:40 / 2.5	-176	0.176	-0.629	141	
Ni / PPY – Co – 40	-222	0.326	<u>-0.3</u> 34	75	

From the table, it is obvious that Ni requires the largest energy input for the given hydrogen production rate (0.379 mW), while Ni / PANI – 5 / 20 requires the smallest energy input (0.175 mW). The trend observed is similar to the one seen in the previous table (5.7) for the exchange current density. The calculations for the hydrogen production

at a fixed overpotential of 150 mV in an imaginary PEM H₂ generator of 50 membranes each of them with 1 m² of surface area operating at standard conditions are presented also in Table 5.8. Again, similarly to the behavior at fixed current density (i.e. hydrogen "production" rate) of 1 mA cm⁻², Ni / PANI 5/20 min yields the best electrocatalytic activity *-i.e.* the amount of hydrogen that could be produced using this catalyst is almost 25 times larger than if Ni/Cu is used.

In the case of Ni / PPY catalysts, it is worth to point out that the difference in catalytic activity is due to the variation in the electrodeposition mechanism. When Ni / PPY catalyst is co-deposited, the actual time of deposition is much shorter than when PPY and Ni are deposited separately. At the end of 40 cycles of co-deposition, the actual PPY deposition is 3 min 20 sec and the total Ni deposition time is 1 min 20 sec, which should then result in a much smaller amount of nickel deposited. However, this catalyst yields much better electrocatalytic activity than the Ni / PPY - 2.5 / 20 catalyst. The amount of hydrogen that could be produced using Ni / PPY - Co - 40 is around 4.7 times larger than if Ni / PPY - 2.5 / 20 is used. The only explanation for the observed discrepancy is related to the increased electroactive surface area of the co-deposited catalyst (and also the amount of catalyst deposited), which was partially discussed in the previous section on the SEM results. Basically, the fundamental reason is related to the mode of the Ni / CP layer formation -i.e. to the increased porosity of the PPY layer. The only way to surpass the catalytical activity obtained using a co-deposition mode by using the other electrodeposition procedure (Ni deposition on a predoposited PPY layer) is by increasing the Ni deposition time. Extending the electrodeposition of Ni to 1 h 40 min results in a better catalytical activity comparable to the Ni / PANI - 5 / 20 catalyst (Figure 5.19, Table 5.8).

The general information obtained from the Tafel polarization data shows that all the Ni / CP catalysts are more active for the HER than the Ni / Cu electrocatalyst. Since the same catalytic material (nickel) is used in all the catalysts, one cannot contribute the increase catalytic activity of the Ni / CP catalysts to the intrinsic nature of the material. Hence, the major reason for the observed superior electrocatalytic activity of the Ni / CP catalysts is related to the increased surface area of the active material (Ni).

5.2.3 Electrochemical impedance spectroscopy

Although the SEM and *dc* Tafel polarization technique gave information on the morphology of the Ni / CP coatings and their overall electrocatalytic activity, the intrinsic nature of these techniques did not give information on the structure of the electrode / electrolyte interface in terms of the charge distribution, electrocatalytic activity centers distribution, and hydrogen adsorption. However, as previously discussed in the EIS section on bimetallic catalysts (section 5.1.4), electrochemical impedance spectroscopy (EIS) technique can offer this information. Hence, to ensure complete characterization of the electrode/electrolyte interface and corresponding processes, EIS measurements were made over six frequency decades, from 10 kHz to 10 mHz at selected overpotentials over the whole range covered in the Tafel plots (ca. from the OCP to the potential of OCP-500 mV). As it will be shown later, the EIS technique revealed new information related to the structure of the electrode/electrolyte interface and the spatial distribution of electroactive centers in the three-dimensional matrix of the Ni / CP electrodes.

Similarly to the previous section that discusses HER results obtained using the dc Tafel technique (section 5.2.2), the EIS technique was also used to study the influence of the Ni and CP deposition time, and the number of cycles in the co-deposition procedure on the resulting electrocatalytic activity, and to study the structure of the Ni / CP / electrolyte interface(s). The following part of the thesis gives examples of Nyquist EIS spectra recorded under the conditions corresponding to various combinations of the Ni and CP (co)deposition times / cycles at specific HER overpotentials. The same trend in the relative electrocatalytic activity was observed in the whole potential range investigated, but due to the clarity of figures, only results recorded at one specific overpotential will be shown. The EIS data obtained at other potentials are presented in Table 5.9 at the end of this section. Also, no detailed discussion will be presented, since the trend observed is quite similar to the one already discussed in the previous section (section 5.2.2). However, a detailed discussion of the guantitative data obtained by EIS measurements, and a physical picture (meaning) of electrode catalytic systems will be presented later in this chapter in relation to the EEC circuits used for the modeling of experimental EIS spectra. For the following discussion it is important to remember that the semicircles presented in Nyquist plots show (e.g. Figure 5.20) a regular closing tendency towards the real impedance axis, which is the typical behavior characteristic of an electrochemical system controlled by a resistive component. Hence, the diameter of the semicircle, which, in the first approximation, can be taken to represent the total resistance to the charge transfer in the HER, is taken as a measure of the catalyst activity. Obviously, a smaller diameter of the semicircle demonstrates better electrocatalytic activity. Since this resistance is inversely related to the current density (i.e. hydrogen production rate), a consistent relationship should exist between linear Tafel polarization plots and the total resistance.





Figure 5.20 shows the influence of the PPY deposition time on the HER electrocatalytic activity of the two corresponding Ni / PPY electrodes. The Ni deposition time was fixed in both cases to 20 min. It can be observed from the figure that the Nyquist plot of the electrode produced with a longer PPY deposition time (5 min) shows a higher resistance (larger semicircle diameter) than the EIS spectrum recorded on the electrode produced with a shorter PPY deposition time (2.5 min). This demonstrates that the catalyst obtained at a shorter PPY deposition time offers a lower resistance to the HER, and hence, higher catalytic activity. This is due to the fact that at shorter deposition times a thinner PPY matrix film is created, and consequently, a larger number of pores protruding to the glassy carbon (GC) substrate are available for Ni deposition, as already explained in the previous section (section 5.2.2). These results are quite in agreement with the behavior observed in linear Tafel polarization (Figure 5.11).

A dramatic decrease in resistance to the HER can be achieved by increasing the Ni deposition time and maintaining a fixed polymer deposition time, as it is demonstrated in Figure 5.21 by the large difference in the semicircle diameters. The catalyst produced a shorter Ni deposition time (20 min) offers resistance to the HER around 6 times larger than the catalyst produced at a longer Ni deposition time (1 h 40 min), making the latter significantly better catalyst for the HER. The explanation for the observed result is related to the surface area of nickel deposited inside and outside the PPY matrix, which is achieved when longer deposition times are used. Hence, the catalyst produced at a longer Ni deposition time (1 h 40 min) offers a considerably larger number of active sites for the reaction, and consequently, an increased catalytic activity can be achieved. These results are quite in agreement with the *dc* Tafel results in Figure 5.12.



Figure 5.21 Nyquist plot showing an ac response in the HER for the catalysts produced by the fixed PPY deposition time (2.5 min) and different PPY deposition times (20 min and 1 h 40 min). Symbols are experimental data and solid lines are modeled data.

In the case of a catalyst produced by co-deposition of Ni and PPY, the Nyquist plot presented in Figure 5.22 shows that the catalyst with higher number of cycles (40) yields a lower resistance to the HER (i.e. smaller semicircle diameter), making it a better HER catalyst in comparison to the one produced with lower number of cycles (20), similarly to the observation presented in Figure 5.13b. This is due to the fact that the catalyst produced with a higher number of cycles offers a higher Ni loading, while at the

same time offering a larger surface area, and consequently, a higher number of active sites for the HER, as explained in previous sections (sections 5.2.1 and 5.2.2).



Figure 5.22 Nyquist plot showing an ac response in the HER for the catalysts produced by the co-deposition of Ni and PPY at 20 and 40 cycles. Symbols are experimental data and solid lines are modeled data.



Figure 5.23 Nyquist plot showing an ac response in the HER for all the different cases studied (influence of PPY deposition time, Ni deposition time, and number of cycles in the co-deposition procedure) on the Ni / PPY electrocatalysts. Symbols are experimental data and solid lines are modeled data.

Figure 5.23 shows the Nyquist EIS spectra of all Ni / PPY electrocatalyts. The trend in the electrocatalytic activity is quite similar to the one observed from the Tafel measurements (Figure 5.14), where the worst electrocatalytic activity is offered by the Ni / PPY – 20 / 5 catalyst, and the best by the Ni / PPY – 1:40 / 2.5 catalyst.

The EIS data obtained on Ni / PANI catalysts are also in very good agreement with the *dc* data recorded on the same electrocatalytic systems. Hence, only a brief discussion of Ni / PANI EIS data will be given in this section, while the detailed discussion is given in the previous section and also applies here.

Figure 5.24 shows that a significant improvement in the electrocatalytic activity of the Ni / PANI catalyst (at a fixed Ni deposition time of 20 min) can be achieved when the deposition time of a PANI matrix is increased -i.e. when the thickness of the PANI film deposited on the GC electrode is increased. The increased PANI matrix thickness offers a larger 3D surface area for the Ni deposition, thus enabling a higher number of Ni electroactive surface sites to be formed, as already discussed. Contrary to the situation, with the influence of PANI deposition time on the resulting electrocatalytic activity, an increase in the Ni deposition time from 20 min to 1 h 40 min does not result in an increase in electrocatalytic activity of the produced catalyst, which is based on a thicker PANI matrix (Figure 5.25). However, when a thinner PANI matrix is used, the results are positive (Figure 5.26) -i.e. the higher loading of Ni results in a significantly higher electrocatalytic activity. This difference occurs because at long PANI deposition times, the polymer layer is thicker and long nickel deposition time results in a blockage of the pores by the growing nickel particles, thus diminishing the total surface area of nickel that could be available for the HER. Simply saying, a benefit of using a thicker PANI matrix that offers more surface area for the Ni deposition is neutralized by too high Ni loading. Although the results presented show that 20 min of Ni deposition gives much better results than 1 h 40 min of Ni deposition, further optimization in terms of both Ni deposition and PANI deposition time is required to achieve a largest possible synergism offered by the combination of PANI and Ni.



Figure 5.24 Nyquist plot showing an ac response in the HER for the catalysts produced by a fixed Ni deposition time (20 min) and different PANI deposition times (2.5 and 5 min). Symbols are experimental data and solid lines are modeled data.



Figure 5.25 Nyquist plot showing an ac response in the HER for the catalysts produced by the fixed PANI deposition time (5 min) and different Ni deposition times (20 min and 1 h 40 min). Symbols are experimental data and solid lines are modeled data.



Figure 5.26 Nyquist plot showing an ac response in the HER for the catalysts produced by the fixed PANI deposition time (2.5 min) and different Ni deposition times (20 min and 1 h 40 min). Symbols are experimental data and solid lines are modeled data.



Figure 5.27 Nyquist plot showing an ac response in the HER for all the different cases studied (influence of PANI deposition time and Ni deposition time) on the Ni / PANI electrocatalysts. Symbols are experimental data and solid lines are modeled data.

Figure 5.27 shows the Nyquist EIS spectra of all Ni/PANI electrocatalyts. The trend in the electrocatalytic activity is also, in this case, quite similar to the one observed from the Tafel measurements (Figure 5.18). The figure shows that the best electrocatalytic activity is achieved with the thicker PANI matrix (5 min) and shorter Ni deposition time (20 min), while significantly lower electrocatalytic activity was observed the PANI matrix was thin (2.5 min) and Ni deposition time short (20 min). The results in Figure 5.27 indicate that the thickness of a PANI layer plays more significant role in the overall electrocatalytic activity of the Ni / PANI catalysts than the Ni loading. Therefore, by increasing the thickness of a PANI layer, even larger electrocatalytic activity could be obtained, assuming that the porosity of the film remains the constant (which is usually the case in a highly porous CP film like PANI, Figure 5.8b). This would, most likely, require further optimization of the Ni deposition time in order to achieve the best possible synergetic effect. However, this is a subject of the future research work in the mentor's laboratory.

In order to obtain a physical picture of the electrode/electrolyte interface and the processes occurring at the catalyst surface, the experimental EIS data were fitted using nonlinear least-squares fit analysis (NLLS) software [52] and the electrical equivalent circuits (EEC) presented in Figure 5.6. Figure 5.28 shows an example of EIS spectra recorded on the Ni / PPY – 20 / 5 electrocatalyst at overpotential -0.135 V. Although the Nyquist plot (Figure 5.28a) shows only one, not completely closed semicircle, the semicircle is somewhat distorted ('stretched') at low frequencies (corresponding to the higher resistance region), thus indicating the existence of a second time constant. This is clearly visible in the Bode plot presented in Figure 5.28b, thus demonstrating that the EIS response of the Ni / PPY – 20 / 5 electrode is, actually, characterized by two time constants.



Figure 5.28 Nyquist (a) and Bode plots (b) showing an *ac* response in the HER at overpotential -135 mV on the Ni/PPY – 20/5 electrode. Symbols are experimental data and solid lines are the modeled data.

The inspection of all the EIS spectra recorded on other five Ni / PPY electrodes also revealed the existence of two time constants. Hence, the two EEC circuits presented in Figure 5.6b and 5.6c were used to model the EIS spectra of Ni / PPY. However, the use of the parallel EEC model (2TP) resulted in a very poor agreement between the experimental and modeled data, while a better agreement was obtained employing the serial model (2TS) (Figure 5.28). On the other hand, the Ni / PANI EIS spectra showed the existence of only one time constant, and the use of simple Randle's circuit (Figure 5.6a) gave a very good fit. The EEC parameters obtained by modeling of the investigated coatings at all the applied overpotentials are presented in Table 5.9.

The example shown in Figure 5.29 demonstrates that as the overpotential increases, there is a significant change in the impedance response. The figure demonstrates that the 2TP EEC model used for the fitting of Ni / PPY spectra can be successfully employed at various overpotentials. The figure also demonstrates that with the increase in overpotential, the HER kinetics also increases, which is demonstrated by the decrease in the diameter of the semicircle in the Nyquist plot, or absolute impedance at low frequencies in the Bode plot. However, by visual inspection it is not possible to determine clearly the trend of the EEC parameters with overpotential. Therefore, a better approach is to inspect the data in Table 5.9 and conclude on the trend in the overpotential behavior. This is quite necessary in order to explain the situation reflected by the recorded EIS spectra *-i.e.* to relate the two time constants on Ni / PPY electrodes to specific physical phenomena (charge-transfer kinetics, hydrogen adsorption, surface porosity).

The EEC parameter values for the Ni / PPY / GC catalysts presented in Table 5.9 show that the behavior of both time constants (τ_1 , CPE₁-R₁, and τ_2 , CPE₂-R₂) depends on the type of electrode used. A close inspection of the values reveals that in each case, the value of CPE₁ remains almost constant, while the value R₁ decreases with overpotential. This confirms that the first time constant is related to the HER kinetics, namely to the capacitance of the double-layer (CPE₁) and charge transfer resistance (R₁).



Figure 5.29 Nyquist Nyquist (a) and Bode plots (b) showing an *ac* response in the HER at different overpotentials for the Ni/PPY -20/5 electrode. Symbols are experimental data and solid lines are modeled data.

On the other hand, the behavior of the second time constant depends on the Ni deposition time. At short Ni deposition times (20 min), the trend of the second time constant is very similar to the trend of the first one -i.e. the value of CPE₂ remains almost constant, while the value R₂ decreases with overpotential. This also confirms that the second time constant is related to the HER kinetics. A lower value of CPE₂ exponent n_2 , compared to exponent n_1 indicates a distortion of the interfacial capacitance, which could be caused by non-equal distribution of surface charges or non-uniformity of the electric field. However, knowing the morphology of the Ni / PPY catalysts obtained by deposition of Ni at short times (Figures 5.9a and 5.9b), we can now easily prescribe the first time constant (τ_1 , CPE₁-R₁) to the response of the Ni above the PPY surface -i.e. Ni that is directly exposed to the electrolyte solution, while the second time constant (τ_2 , CPE₂-R₂) represents the response of Ni embedded in the PPY matrix. Since the outer Ni catalytic centers are directly exposed to the electric field created between the working and counter electrodes, the distribution of this field could expected to be uniform. However, the electric field between the counter electrode and the Ni surface embedded in the PPY matrix is quite nonuniform due to the influence of the PPY matrix, which physically interacts with the electric field. Some (di)electric influence of the PPY matrix could also be expected.

In the case of Ni / PPY co-deposited coatings, both time constants are also related to the HER kinetics, similarly to the above situation with Ni / PPY at short Ni deposition times. However, the situation with Ni / PPY electrodes obtained at long Ni deposition times (1h 40min) is quite different. While the first time constant (τ_1 , CPE₁-R₁) is still related to the HER kinetics, as discussed above, the second time constant (τ_2 , CPE₂-R₂) does not change with overpotential (Table 5.9). This indicates that the second time constant is related to the electrode surface porosity response, which is in agreement with the literature description of the 2TS EEC model used in the analysis [23,41,59]. This also shows that the Ni layer above the PPY matrix dominates the EIS response when compared to the response of a part embedded into the PPY matrix. The reason for this could be due to the significant change in the morphology of the Ni layer above the PPY matrix, which is evidenced by the comparison of SEM images presented in Figure 5.30. The deposition of Ni at longer times results in an increase in the surface

area of Ni above the PPY matrix layer, which significantly contributes to the increase in the kinetics of the HER, as it was demonstrated previously (Figure 5.23).



Figure 5.30 Ni deposits obtained by electrodeposition of Ni in a PPY matrix. The PPY matrix was pre-deposited for 5 min, while the electrodeposition time for Ni was (a) 1 h 40 min, and (b) 20 min.

The EIS behavior of Ni / PANI catalysts differ significantly from the behavior recorded on Ni / PPY catalysts. Namely, both Nyquist and Bode plots of Ni / PANI electrodes showed the existence of only one time constant. Hence, the experimental spectra were fitted with the one time constant model that describes the response of a system governed only by the charge-transfer kinetics (Figure 5.6a) [71,75]. The agreement between the modeled and experimental spectra is very good, as shown in Figures 5.24 to 5.27.

Besides using the EEC data and EEC circuit models to describe the structure of a catalyst/electrolyte surface and the corresponding surface charge distribution, the charge-transfer resistance values presented in Table 5.9 were used to compare a relative electrocatalytic activity of the Ni / CP catalysts, and also to compare the resulting trend with overpotential to the trend observed with Tafel curves (Figure 5.19). In order to do this, a semi-logarithmic plot of the dependence of the HER rate versus applied overpotential is presented in Figure 5.31 for the same catalysts presented in Figure 5.19. The approach used to plot the curves was already described in Section 5.1.3. The trend of curves in Figure 5.31 is very similar to the trend obtained by dc polarization (Figure 5.19). The Ni coating displays the lowest activity, while the Ni / PANI – 20 / 5 coating again shows the highest activity, followed, in a decreasing order of activity, by Ni / PPY –

1:40 / 2.5, and Ni / PPY – Co – 40. The curves show a Tefel region at overpotentials more positive of -400 mV, while a gradual change to lower Tafel slopes is observed at higher overpotentials, in accordance with the *dc* curves presented in Figure 5.19. This trend was already discussed in relation to Figure 5.19.



Figure 5.31 Comparison of the electrocatalytic activity of Ni / CP electrocatalysts and the Ni / Cu catalyst shown as a logarithmic dependence of $(R_1 + R_2)^{-1}$ on overpotential. The data was obtained by modeling EIS spectra recorded on the corresponding electrocatalysts.

η^-	R _{el}	CPE ₁	n,	R_1	CPE ₂		R_2		
(V)	(Ω)	(F s ⁿ⁻¹ cm ⁻²)		$(\Omega \text{ cm}^2)$	(F s ⁿ⁻¹ cm ⁻²)		$(\Omega \text{ cm}^2)$		
Ni / PPY - 20 / 5									
-0.115	4.37	1.75E-04	1.00	789.9	4.19E-04	0.73	860.1		
-0.135	4.44	1.75E-04	1.00	716.5	5.04E-04	0.72	873.8		
-0.155	4.57	1.73E-04	1.00	622.1	4.89E-04	0.73	716.0		
-0.175	4.64	1.61E-04	1.00	510.8	5.28E-04	0.72	556.3		
-0.195	4.82	1.66E-04	1.00	374.3	4.76E-04	0.73	420.2		
-0.215	4.90	1.58E-04	1.00	293.0	5.04E-04	0.73	299.3		
-0.235	4.87	1.60E-04	1.00	214.9	4.79E-04	0.73	237.8		
-0.260	4.98	1.53E-04	1.00	161.6	4.88E-04	0.73	175.4		
-0.285	5.08	1.61E-04	1.00	114.8	4.15E-04	0.75	141. 9		
-0.335	5.06	1.49E-04	0.97	80.7	5.16E-04	0.74	73.7		
-0.385	5.05	1.74E-04	1.00	32.4	3.46E-04	0.76	69.3		
-0.435	<u>5.07</u>	1.83E-04	1.00	19.1	3.03E-04	0.77	47.4		
			Ni / PPY	- 1:40 / 5					
-0.135	3.75	4.50E-04	0.92	158.22	1.54E-03	0.62	7.03		
-0.155	3.98	4.02E-04	0.93	152.11	1.62E-03	0.61	7.63		
- 0.175	4.10	3.79E-04	0.94	129.90	1.64E-03	0.61	7.97		
-0.195	4.47	3.63E-04	0.95	106.86	1.50E-03	0.61	8.25		
-0.215	4.26	3.68E-04	0.95	82.31	1.52E-03	0.62	8.61		
-0.235	4.33	3.62E-04	0.93	67.57	9.84E-04	0.66	6.77		
-0.260	4.82	3.69E-04	0.93	49.38	6.75E-04	0.69	6.07		
-0.285	4.60	3.71E-04	0.93	35.58	6.81E-04	0.69	6.43		
-0.310	4.58	3.89E-04	0.93	24.75	8.53E-04	0.67	6.75		
-0.335	4.84	3.99E-04	0.93	18.19	7.80E-04	0.68	7.13		
-0.385	4.55	4.57E-04	0.89	11.70	5.89E-04	0.71	5.09		
-0.435	4.55	4.45E-04	0.99	4.78	5.82E-04	0.70	7.60		
-0.535	5.16	4.52E-04	0.89	4.03	3.36E-04	0.76	3.98		
-0.585	5.09	3.71E-04	0.99	2.10	2.27E-04	0.79	4.94		

Table 5.9 EEC parameters obtained by fitting EIS experimental spectra recorded at various overpotentials on the investigated Ni / CP electrocatalysts using the EEC models presented in Figure 5.6.
η	R_{el}	CPE₁	n	R1	CPE₂	n	R_2	
(∨)	(Ω)	(F s ^{<i>n-1</i>} cm ⁻²)	111	$(\Omega \text{ cm}^2)$	(F s ⁿ⁻¹ cm ⁻²)	112	$(\Omega \text{ cm}^2)$	
Ni / PPY - 20 / 2.5								
-0.085	3.77	1.36E-04	0.89	1262.8	5.27E-03	0.50	316.03	
-0.095	4.12	1.37E-04	0.90	1278.9	3.90E-03	0.54	465.12	
-0.115	4.19	1.37E-04	0.90	1129.8	3.54E-03	0.55	415.65	
-0.135	4.21	1.35E-04	0.91	935.7	3.67E-03	0.54	289.17	
-0.155	4.20	1.34E-04	0.90	766.4	4.88E-03	0.52	183.26	
-0.175	4.33	1.34E-04	0.90	586.3	4.82E-03	0.52	147.78	
-0.195	4.40	1.34E-04	0.90	435.9	5.11E-03	0.52	114.55	
-0.215	4.40	1.35E-04	0.89	346.6	7.46E-03	0.49	61.59	
-0.235	4.65	1.33E-04	0.89	254.7	7.83E-03	0.48	61.35	
-0.260	4.55	1.36E-04	0.89	171.0	6.66E-03	0.50	32.15	
-0.285	4.75	1.35E-04	0.90	110.0	4.97E-03	0.52	33.73	
-0.310	4.55	1.36E-04	0.89	79.3	6.49E-03	0.51	20.28	
-0.335	4.32	1.36E-04	0.88	57.0	8.90E-03	0.47	12.24	
-0.360	4.09	1.35E-04	0.88	82.0	1.03E-02	0.46	12.96	
-0.385	4.29	1.36E-04	0.88	30.0	5.64E-03	0.52	7.29	
-0.435	4.80	1.35E-04	0.88	17.0	3.57E-03	0.56	4.68	
-0.535	5.10	1.57E-04	0.93	4.7	4.65E-04	0.72	5.57	
-0.585	5.17	1.28E-04	0.84	7.7	1.19E-03	0.71	0.46	
Ni / PPY - 1:40 / 2.5								
-0.115	4.12	5.22E-04	0.93	146.97	9.06E-04	0.67	0.90	
-0.135	4.33	4.92E-04	0.94	141.90	1.33E-03	0.64	0.92	
-0.155	4.54	4.59E-04	0.95	121.69	2.01E-03	0.60	0.96	
-0.175	4.70	4.44E-04	0.95	95.80	1.86E-03	0.61	0.96	
-0.195	4.47	4.35E-04	0.95	72.17	1.32E-03	0.65	0.88	
-0.215	4.90	4.33E-04	0.95	52.34	2.20E-03	0.59	0.93	
-0.235	5.04	4.41E-04	0.95	37.30	1.33E-03	0.65	0.88	
-0.260	5.00	4.44E-04	0.95	24.28	1.77E-03	0.62	0.89	
-0.285	5.08	4.58E-04	0.95	15.81	1.67E-03	0.62	0.86	
-0.310	4.99	4.71E-04	0.94	10.59	7.67E-04	0.70	0.78	
-0.335	4.60	4.87E-04	0.94	7.22	5.17E-04	0.73	0.78	
-0.360	5.49	4.90E-04	0.94	9.88	1.08E-03	0.70	0.67	
-0.385	4.87	5.20E-04	0.93	3.70	5.50E-04	0.73	0.75	
-0.435	5.57	5.11E-04	0.92	2.35	1.38E-04	0.86	0.61	

Table 5.9 cont.

n	R_{el}	CPE1	n.	R₁	CPE₂	n.	R_2
/	(Ω)	(F s ⁿ⁻¹ cm ⁻²)	111	$(\Omega \text{ cm}^2)$	(F s ⁿ⁻¹ cm ⁻²)		$(\Omega \text{ cm}^2)$
			Ni / PP)	(- Co - 20			
-0.135	4.42	4.92E-04	0.88	318.70	1.54E-02	1.00	45.90
-0.155	4.22	4.70E-04	0.88	277.95	1.91E-02	0.8 9	49.08
-0.175	4.19	4.71E-04	0.87	181.90	5.79E-03	0.86	51.13
-0.195	4.21	5.33E-04	0.88	83.27	1.69E-03	0.86	71.16
-0.215	4.24	6.32E-04	0.89	35.51	9.51E-04	0.86	69.92
-0.235	4.28	5.98E-04	0.90	24.84	9.39E-04	0.86	49.86
-0.260	4.30	4.76E-04	0.90	21.97	1.43E-03	0.84	27.30
-0.285	4.33	4.13E-04	0.90	19.62	2.69E-03	0.82	13.30
-0.310	4.35	3.92E-04	4 0.90 14.44 4.17E-03		0.79	7.71	
-0.335	4.28	3.65E-04	0.94	7.62	3.10E-03	0.75	6.96
-0.360	4.36	3.76E-04	0.90	14.36	6.48E-03	0.78	6.12
-0.385	4.19	3.17E-04	0.97	3.66	5.72E-03	0.68	2.93
-0.435	4.49	4.36E-04	4.36E-04 0.88 2.99		-	-	-
-0.535	4.63	5.35E-04	5.35E-04 0.87 1.03		-	-	-
-0.585	4.63	5.67E-04	0.86	0.71	-	-	-
-0.635	4.58	6.53E-04	E-04 0.83 0.54 -		-	-	
Ni / PPY - Co - 40							
-0.155	6.26	7.27E-04	0.92	175.97	3.07E-02	1.00	28.11
-0.175	5.32	6.66E-04	0.91	169.49	6.65E-02	0.92	22.11
- 0.195	5.15	6.22E-04	0.91	130.05	4.66E-02	0.81	13.57
-0.215	5.22	6.32E-04	0.91	122.25	1.47E-02	0.88	18.78
-0.235	5.27	6.60E-04	0.91	43.90	3.35E-03	0.8 9	19.37
-0.260	5.63	6.42E-04	0.92	26.74	3.29E-03	0.89	12.33
-0.285	5.42	5.98E-04	0.92	18.20	5.33E-03	0.85	6.25
-0.310	4.92	5.28E-04	0.97	10.37	7.59E-03	0.72	4.25
-0.335	5.03	6.00E-04	0.97	5.14	4.01E-03	0.77	4.06
-0.360	5.22	5.83E-04	0.94	8.65	6.21E-03	0.78	4.02
-0.385	3.86	5.76E-04	0.93	3.56	1.92E-01	0.32	1.06
-0.435	4.15	3.75E-02	0.48	0.75	5.50E-04	0.97	1.50
-0.535	4.05	2.71E-02	0.47	0.42	6.51E-04	0.96	0.54
-0.585	3.50	5.57E-02	0.33	0.49	6.28E-04	0.96	0.37
-0.635	5.18	1.15E+00	1.00	0.06	1.29E-03	0.84	0.39

Table 5.9 cont.

n	R_{el}	R _{el} CPE ₁ n.		R₁	CPE ₂	n	R_2				
1	(Ω)	(F s ^{<i>n-1</i>} cm ⁻²)	111	$(\Omega \text{ cm}^2)$	(F s ^{<i>n-1</i>} cm ⁻²)	112	$(\Omega \text{ cm}^2)$				
	Ni / PANI - 20 / 5										
-0.115	5.38	3.85E-04	0.93	98.07	-		_				
-0.135	5.60	3.61E-04	0.93	80.67	-	-	-				
-0.155	5.80	3.45E-04	0.93	64.09	-	-	-				
-0.175	6.10	3.34E-04	0.94	50.15	-	-	-				
-0.195	6.28	3.25E-04	0.94	38.74	-	-	-				
-0.215	6.36	3.23E-04	0.94	29.67	-	-	-				
-0.235	6.60	3.21E-04	0.94	22.51	-	-	-				
-0.260	6.63	3.26E-04	0.94	16.08	-	-	-				
-0.285	6.63	3.28E-04	0.94	11.43	-	-	-				
-0.310	6.69	3.40E-04	0.94	8.23	-	-	-				
-0.335	6.76	3.38E-04	0.95	5.94	-	-	-				
-0.360	6.67	3.38E-04	0.94	7.97	-	-	-				
-0.385	6.69	3.61E-04	0.94	3.37	-	-	-				
-0.435	6.59	3.65E-04	0.94	2.04	-	-	-				
-0.535	7.09	3.59E-04	0.96	0.90	-	-	-				
-0.585	6.97	3.74E-04	0.96	0.67	-	-	-				
			Ni / PAN	ll - 1:40 / 5	. –						
-0.135	7.93	8.79E-04	0.96	70.79	-	-	-				
-0.155	8.64	8.01E-04	0.97	72.44	-	-	-				
-0.175	8.77	7.60E-04	0.97	63.16	-	-	-				
-0.195	8.70	7.30E-04	0.98	50.17	-	-	-				
-0.215	8.84	7.09E-04	0.98	37.83	-	-	-				
-0.235	8.60	7.08E-04	0.98	28.76	-	-	-				
-0.260	9.24	7.13E-04	0.99	20.25	-	-	-				
-0.285	8.87	7.21E-04	0.99	14.22	-	-	-				
-0.310	8.71	7.34E-04	0.99	10.0 1	-	-	-				
-0.335	9.30	7.14E-04	1.00	6.94	-	-	-				
-0.360	8.55	7.43E-04	0.99	10.18	-	-	-				
-0.385	9.16	7.57E-04	1.00	3.61	-	-	-				
-0.435	9.17	8.02E-04	1.00	2.01	-	-	-				
-0.535	9.30	9.13E-04	1.00	0.74	-	-	-				
-0.585	8.53	8.11E-04	1.00	0.53	-	-	-				
-0.635	8.58	8.44E-04	1.00	0.37	-	-	-				

Table 5.9 cont.

|--|

n	R _{el}	CPE₁	2	R_1	CPE ₂	n	R ₂			
	(Ω)	(F s ⁿ⁻¹ cm ⁻²)	111	$(\Omega \text{ cm}^2)$	(F s ^{<i>n-1</i>} cm ⁻²)	112	$(\Omega \text{ cm}^2)$			
Ni / PANI - 20 / 2.5										
-0.135	5.24	6.93E-04	0.89	303.11	-	-	-			
-0.155	5.61	6.35E-04	0.89	342.21	-	-	-			
-0.175	5.60	5.93E-04	0.90	328.61	-	-	-			
-0.195	5.68	5.74E-04	0.90	271.49	-	-	-			
-0.215	5.50	5.67E-04	0.90	208.76	-	-	-			
-0.235	5.61	5.62E-04	0.90	160.68	-	-	-			
-0.260	5.49	5.71E-04	0.90	113.99	-	-	-			
-0.285	5.39	5.77E-04	0.90	77.74	-	-	-			
-0.310	5.31	5.83E-04	0.90	51.51	-	-	-			
-0.335	5.20	5.95E-04	0.90	32.93	-	-	-			
-0.385	5.26	6.01E-04	0.90	13.13	-	-	-			
-0.435	5.20	5.91E-04	0.91	5.16	-	-	-			
-0.535	5.24	5.97E-04	0.91	1.10	-	-	-			
-0.585	5.32	6.00E-04	0.92	0.65	-	-	-			
-0.635	5.27	5.91E-04	0.92	0.47	-	-				
			Ni / PANI	- 1:40 / 2.5						
-0.155	5.33	8.14E-04	0.95	106.64	-	-	-			
-0.175	4.85	7.68E-04	0.95	95.10	-	-	-			
-0.195	5.11	7.41E-04	0.95	74.80	-	-	-			
-0.215	5.41	7.30E-04	0.95	56.66	-	-	-			
-0.235	5.50	7.28E-04	0.96	41.96	-	-	-			
-0.260	5.54	7.36E-04	0.96	28.61	-	-	-			
-0.285	5.62	7.43E-04	0.96	19.14	-	-	-			
-0.310	5.39	8.02E-04	0.95	12.86	-	-	-			
-0.335	5.11	8.04E-04	0.95	8.49	-	-	-			
-0.360	6.61	7.71E-04	0.96	12.54	-	-	-			
-0.385	5.36	8.33E-04	0.95	4.20	-	-	-			
-0.435	5.56	8.34E-04	0.96	2.19	-	-	-			
-0.535	5.34	7.95E-04	0.96	0.76	-	-	-			
-0.585	4.92	7.34E-04	0.95	0.55	-	-	-			
-0.635	4.86	1.00E-03	0.90	0.48		-				

5.2.4 Potential relaxation behavior

One of the best approaches used to assess the real surface area of the catalyst is to obtain the information on the value of double layer capacitance. This value can be evaluated by different techniques, and electrochemical impedance spectroscopy (EIS) has been shown to be best for this purpose [13,41,64]. Another technique presented in [24,62] is based on potential-decay measurements. This part of the thesis presents results obtained by this technique, with the purpose to verify the information on the surface roughness obtained by EIS. Ni / CP coatings were used for this purpose, since they represent a much more complex surface catalyst system, compared to Ni / Cu coatings; and the interpretation of the corresponding EIS data is, thus, somewhat more complex. It will be shown that both techniques give comparable results related to the assessment of the true, electrochemically available surface area for the HER.

First, a brief explanation of the potential-decay technique is given in the following text. The resulting capacitance *C* at the electrode/electrolyte interface for the HER is composed of two elements: the double layer capacitance C_{dl} (F cm⁻²) and the pseudocapacitance C_{ϕ} (F cm⁻²).

$$C = C_{dl} + C_{\phi} \tag{5.6}$$

The latter, C_{φ} , is related to the hydrogen adsorption on the electrode surface and has to be distinguished from C_{dl} . Hence, potential-relaxation transients are recorded over a very short time range -i.e. during the double-layer discharge process, which is not influenced by hydrogen adsorption. The pseudocapacitance is expressed by:

$$C_{\phi} = q \frac{\partial \theta}{\partial \eta} \tag{5.7}$$

where q (C cm⁻²) is the charge required to form a monolayer of the adsorbed hydrogen intermediate and θ is the surface coverage fraction. η corresponds to the overpotential ($\eta = E - E_{eq}$). During the cathodic polarization of the electrode, a Faradic current density crosses the electrode/electrolyte interface and is given by the Butler-Volmer equation:

$$j(\eta) = j_o \exp(\alpha f \eta)$$
(5.8)

where $f = \frac{F}{RT}$, j_o is the exchange current density (A cm⁻²). After stopping the polarization, the relation between the prior steady state and following potential-relaxation behaviour is provided by:

$$-C\frac{d\eta}{dt} = j(\eta) = j_o \exp(\alpha f\eta)$$
(5.9)

were *C* is the interfacial capacitance approximated to C_{dl} for a short time range. Assuming that *C* is constant, integration of Equation (5.9) gives:

$$\eta(t) = a - b\log(t + \tau) \tag{5.10}$$

with

$$a = -b \log\left(\frac{2.3j_o}{bC}\right) \tag{5.11}$$

$$b = \frac{2.3}{\alpha f} \tag{5.12}$$

$$\tau = \frac{bC}{2.3j_{(t=0)}}$$
(5.13)

Then, the interfacial capacitance (in that case C_{dl}) can be calculated from Equation (5.9):

$$C = \frac{j_{(t=0)}}{\begin{pmatrix} -d\eta \\ dt \end{pmatrix}_{t=0}}$$
(5.14)

and the initial potential-decay slope can be determined by differentiating Equation (5.10) with respect to time *t* and giving:

$$\left(\frac{d\eta}{dt}\right)_{t=0} = -\frac{b}{2.3\tau}$$
(5.15)

Using the above outlined procedure, it is possible to evaluate the real surface area of the coating, which is the ratio between the C_{dl} and the double layer capacitance (20 μ F c m⁻²) of a smooth metal electrode [13,71].

In order to assess the double layer capacitance C_{dl} reliably, potential-relaxation transients were recorded from eleven values of overpotentials η (from the OCP to OCP + 0.2 V in the cathodic region) along the Tafel slope, after interruption of established steady state currents. This experiment was performed on Ni / PPY – 20 / 5, Ni / PANI – 20 / 5 and Ni / PPY – Co – 20 electrode coatings. The electrolyte used was again 0.5 M H₂SO₄, which is sufficient to get facile electrochemical access to virtually all of the inner surface area of the porous electrode. Then, the η vs. *t* data are fitted to Equation (5.10), as explained previously, by means of a non-linear least squares fitting procedure, using Excel "solver" software to get best values for the constants *a*, *b* and *t* for each $\eta(t)$ curve. Hence, the potential-decay slope can be calculated from Equation (5.15) and *C*, which is C_{dl} , can be determined using Equation (5.14). A good fitting of the experimental relaxation data for all the coatings was obtained (see Figure 5.32) and the calculated parameters are presented in Appendix *A* in Table A.1. The real surface area and roughness factor (real/geometric surface area ratio) was evaluated using the average value obtained for the C_{dl} of each coating.

After the potential relaxation experiments, EIS was recorded at 2 different overpotentials for the Ni / PANI – 5 / 20 coating and at 3 different overpotentials for the Ni / PPY coatings. The experimental data was modeled using the same ECC circuits employed in section 5.2.3 for the equivalent electrocatalysts. The EEC parameters obtained at all the applied overpotentials are presented in Table A.2 in Appendix *A*. The value of the double layer capacitance was then calculated using the approach already discussed in section 5.1.5. Table 5.10 compares values obtained using both techniques, and it can be seen that the real surface area and roughness factor were calculated to compare them with the values obtained using the potential relaxation technique. From Table 5.10 it can be seen that the calculated values using these two different techniques are quite similar.



Figure 5.32 Overpotential vs. time plots for the HER at Ni / PANI – 20 / 5 electrode recorded after interruption of steady state currents for 8 overpotentials. Symbols are experimental data and solid lines are modeled data.

Table 5	.10	Real	surface	e area	and	corres	ponding	surface	roughness	values	for	the
investiga	ated	Ni / (CP / GC	catal	/tic c	oatings	calculate	ed from	the potentia	I-relaxat	ion	and
EIS data	a .											

	Potential	Relaxation	EIS		
Catalyst	A _{real} (cm ²)	σ	A_{real} (cm ²)	σ	
Ni / PANI - 20 / 5	1.4±0.2	8.1±1.3	1.3±0.1	7.7±0.4	
Ni / PPY - 20 / 5	1.3±0.2	7.6±0.9	1.6±0.0	9.6±0.2	
Ni / PPY - Co - 20	1. <u>8±0.2</u>	10.8±1.1	<u>1.4±0.0</u>	8.5±0.2	

The roughness factor values of all the different Ni / CP electrodes are two-tothree times higher than the value obtained when nickel was deposited on a Cu N substrate (Table 5.5), and significantly higher then the value obtained by Lasia [52] for polycrystalline nickel (σ = 1.7). Thus, it can be seen that by using CP matrices the surface roughness of the active catalyst can be increased, and thus, the amount of hydrogen produced. However, it has to be emphasized that the Ni / CP results presented in the thesis are the first reported attempts to use CPs as pattering templates (matrices) for electroddeposition of nickel for the HER and, hence, further optimization is required to obtain best performances of the system.

CHAPTER 6

6. CONCLUSIONS

This thesis discusses results on the development of Ni-based electrocatalysts for hydrogen evolution in an acidic medium. This topic has a great importance for the development of a PEM-type hydrogen generator, as a global initiative for the development of clean sustainable energy systems.

A number of experimental techniques were used in research: the electrocatalytic activity of the catalysts was investigated using electrochemical techniques of linear *dc* polarization (Tafel), electrochemical impedance spectroscopy (EIS), and potential-decay. The chemical composition of the catalyst coatings was determined using inductively coupled plasma (ICP), while the structural composition and the surface morphology was investigated using X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively.

The first part of the thesis discusses the results of the influence of alloying nickel with left-hand side transition metals (Fe, Mo, W) on the electrocatalytic activity in hydrogen evolution, while the second part of the thesis discusses the results on the development of Ni electrocatalysts using conductive polymers, PPY and PANI, as catalysts pattering matrices.

6.1 Ni-M (M = Mo, W, Fe) Electrocatalysts

The XRD analysis revealed that Ni, NiW-1 and NiFe-2 electrocatalytic coatings are crystalline, while NiMo-1, NiMo-2 and NiFe-1 coatings are amorphous. The main phase in all the coatings is the nickel f.c.c. structure, with the second element incorporated into the structure. It was noticed that the increase in crystallinity can contribute to the increased electrocatalytic activity in the HER. The SEM analysis was in accordance with the XRD analysis. It revealed that the NiMo coatings offer the highest 3D surface area among the investigated coatings. The electron diffraction spectroscopy analysis confirmed that the alloy constituents in all the coatings are uniformly distributed on the catalysts' surface.

Tafel and EIS results presented in the thesis clearly demonstrate that alloying nickel with left-hand side transition metals (Fe, Mo, W) results in an increased electrocatalytic activity in the HER when compared to pure nickel. Two effects were found to be responsible for the observed behavior; the increase in surface roughness and the increase in intrinsic activity of the material. All bimetallic coatings were found to offer higher overall electrocatalytic activity than pure nickel, and the prevailing factor that contributes to this was found to be the increased surface roughness. NiMo-1 (Ni73Mo) was found to yield the highest overall electrocatalytic activity among the investigated materials. On the other hand, NiW-1 (Ni_{3.4}W) was found to yield the highest intrinsic electrocatalytic activity, which was postulated to be due to the modification of the electron density in the d-shell upon alloying nickel with tungsten in a way that favors the HER kinetics. This is also supported by the observed increase in intrinsic electrocatalytic activity of the two NiMo coatings when compared to pure nickel. Although both NiFe coatings yielded a better overall electrocatalytic activity than pure nickel, their intrinsic electrocatalytic activity was lower than of pure nickel. This is most likely due to the presence of an oxide film on the catalysts surface.

The results presented demonstrate that the design of high-activity HER electrocatalysts could be based on the increase of both active surface area and intrinsic activity of the material. The latter can be achieved by a proper choice of experimental conditions for the material preparation (*e.g.* using methods for the synthesis of nano-particles, such as colloidal or plasma-assisted method), the increase in the intrinsic activity can be achieved by a proper combination of left- and right-hand side transition metals. Three theories that explain the HER intrinsic activity of bimetallic alloys were discussed in the thesis, and correlated with the experimental results presented. Although all three outlined theories give a background for the design of intrinsically active HER electrocatalysts, none of them offers definite general answers that could be used for the design directions, and further meticulous and systematic investigation of the influence of all observed effects (electron density, surface diffusion, surface strain, crystallinity, etc.) on the materials' electrocatalytic activity in the HER is needed.

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6.2 Ni / Conducting Polymer Electrocatalysts

It was shown that pattering a glassy carbon electrode surface with conducting polymers (PPY and PANI) offers a convenient method of increasing the surface area of the nickel electrocatalytic coating. The influence of a CP matrix thickness (*i.e.* CP deposition time) and Ni loading (*i.e.* Ni deposition time) on the overall HER electrocatalytic activity of the electrode was investigated. It was demonstrated that Ni / CP electrocatalysts offer significantly higher HER electrocatalytic activity when compared to a classical nickel layer electrodeposited on a copper substrate. This was explained on the basis of the increased surface roughness (area) of the Ni / CP coatings.

It was concluded that the morphology of the electrodeposited CP matrix greatly influences the overall electrocatalytic activity of the Ni catalyst layer. The PANI matrix was found to offer much more porous structure than the PPY matrix, which enabled a higher Ni surface area to be obtained per amount of nickel loaded. This yielded a higher overall HER electrocatalytic activity and a highly porous Ni-layer structure suitable for the design of PEM-type membrane-electrode-assemblies.

The HER electrocatalytic activity of Ni / PPY coatings greatly depended on the method of the catalytic layer preparation and the loading of PPY and Ni. The highest activity was obtained for the short PPY deposition time and long Ni deposition time, while the lowest activity was obtained for the layer prepared by long PPY and short Ni deposition times. The difference was explained on the basis of PPY layer porosity and the amount (i.e. surface area) of Ni created. It was also shown that the co-deposition method offers a significant increase in the Ni dispersion and thus increased electrocatalytic activity. Two surface regions of Ni were found to be active towards HER: Ni islands directly exposed to the electrolyte solution (1st region), connected to the GC substrate through Ni 'stalks' embedded into a PPY matrix (2nd region). It was postulated that the mass-transfer limitations located at the Ni/PPY interface (in the interior Ni / PPY layer) are responsible for the decrease in the HER rate at high overpotentials.

The results on Ni / PANI electrocatalysts also revealed that the overall HER activity of these catalyst depends on both the thickness of the PANI matrix and Ni loading. However, the thickness of the PANI matrix was found to be a prevailing factor. The highest HER electrocatalytic activity was found to be offered if a thickness of a PANI

matrix is large and Ni loading is low, while a catalyst with a thin PANI matrix and low Ni loading offered the lowest HER electrocatalytic activity. The HER was found to be entirely kinetically controlled in the whole overpotential region studied, with the absence of mass transfer limitations as on Ni / PPY electrocatalysts. This is due to the large difference in the three-dimensional structure of the two catalysts.

Overall, the two best Ni / CP catalysts from each group (PPY and PANI) were found to offer very comparable HER electrocatalytic activity at low overpotentials, relevant to the operation of PEM hydrogen generators. Only at high overpotentials the Ni catalyst with a PANI matrix was found to offer a higher activity, which is due to the favorable 3D porous structure of the Ni / PANI layer.

The applicability of EIS in the determination of the real surface area of the HER Ni / CP catalysts was verified using a potential-decay technique. It was found that both techniques offer very comparable results.

REFERENCES

- 1. S. Dun, Int. J. Hydrogen Energy, 27 (2002) 235.
- 2. T. Hijikata, Int. J. Hydrogen Energy, 27 (2002) 115.
- 3. P. Kruger, Int. J. Hydrogen Energy, 25 (2000) 395.
- 4. C. Mitsugi, A. Harumi, F. Kenzo, Int. J. Hydrogen Energy, 23 (1998) 159.
- 5. W. Kreuter, H. Hofmann, Int. J. Hydrogen Energy, 23 (1998) 661.
- 6. O. Ulleberg, Int. J. Hydrogen Energy, 28 (2003) 21.
- 7. J. Ivy, 'Summary of Electronic Hydrogen Production', *Milestone Completion Report*, National Renewable Energy Laboratory, Colorado USA (2004).
- 8. F. Fantes, Harvard Science Review, winter (2002).
- P. Millet, F. Andolfatto, R. Durand, Int. Journal of Hydrogen Energy, 21-2 (1996) 87.
- 10. R.G.M. Crockett, M. Newborough, D.J. Highgate, S.D. Probert, *Applied Energy*, 51 (1995) 249.
- 11. P. Millet, R. Durand, M. Pineri, Int. Journal of Hydrogen Energy, 15-4 (1990) 245.
- 12. S.D. Han, K.B. Park, R. Rana, K.C. Singh, *Indian Journal of Chemistry*, 41 (2002) 245.
- 13. L. Chen, A. Lasia, J. Electrochem. Soc., 138 (1991) 3321.
- 14. P. Los, A. Rami, A. Lasia, J. Appl. Electrochem., 23 (1993) 135.
- 15. C. Hitz, A. Lasia, J. Electroanal. Chem., 500 (2001) 213.
- 16. B.E. Conway, G. Jerkiewicz, *Electrochim. Acta*, 45 (2000) 4075.
- 17. J.G. Highfield, E. Claude, K. Oguro, *Electrochim. Acta*, 44 (1999) 2805.
- 18. H. Ezaki, M. Morinaga, S. Watanabe, *Electrochim. Acta*, 38 (1993) 557.
- 19. H. Ezaki, M. Morinaga, S. Watanabe, J. Saito, *Electrochim. Acta*, 39 (1994) 1769.
- H. Shibutani, T. Higashijima, H. Ezaki, M. Morinaga, K. Kikuchi, *Electrochim. Acta*, 43 (1998) 3235.
- 21. M. Metikos-Hukovic, A. Jukic, *Electrochim. Acta*, 45 (2000) 4159.
- 22. R. Karimi Shervedani, A. Lasia, J. Appl. Electrochem., 29 (1999) 979.
- 23. B. Losiewicz, A. Budniok, E. Rowinski, E. Lagiewka, A. Lasia, *Int. J. Hydrogen Energy*, 29 (2004) 145.
- R. Simpraga, G. Tremiliosi-Filho, S.Y. Qian, B.E. Conway, J. Electroanal. Chem., 424 (1997) 141.

- 25. H. Ezaki, T. Nambu, M. Morinaga, M. Udaka, K. Kawasaki, Int. J. Hydrogen Energy, 21 (1996) 877.
- 26. S. Tanaka, N. Hirose, T. Tanaki, Int. J. Hydrogen Energy, 25 (2000) 481.
- 27. M.M. Jaksic, *Electrochim. Acta*, 45 (2000) 4085.
- 28. M.M. Jaksic, Solid State Ionics, 136-137 (2000) 733.
- 29. R.K. Shervedani, A. Lasia, J. Electrochem. Soc., 144 (1997) 2652.
- 30. W. Hu, Int. J. Hydrogen Energy, 25 (2000) 111.
- P. Dabo, L. Brossard, H. Ménard, P. Tremblay, J. Appl. Electrochem., 28 (1998) 601.
- H. Ezaki, T. Nambu, M. Morinaga, M. Udaka, K. Kawasaki, Int. J. Hydrogen Energy, 21-10 (1996) 877.
- 33. M.H. Miles, M.A. Thomason, J. Electrochem. Soc., 123 (1976) 1459.
- 34. B.E. Conway, J.O'M. Bockris, J. Chem. Phys., 26 (1957) 532.
- 35. L.I. Krishtalik, in: P. Dalahay, C. Tobias (Eds.), 'Advances in Electrochemistry and Electrochemical Engineering', Vol. 7, Interscience, New York, 1970, p.283.
- 36. S. Trasatti, J. Electroanal. Chem., 39 (1972) 163.
- 37. S. Trasatti, J. Chem. Soc. Faraday Trans., 68 (1972) 229.
- M. Kondoh, N. Yokoyama, C. Inazumi, S. Maezawa, N. Fujiwara, Y. Nishimura, K. Oguro, H. Takenaka, J. NewMat. Electrochem. Sys., 3 (2000) 61.
- 39. X. Wang, I.M. Hsing, P.L. Yue, J. Power Sources, 96 (2001) 282.
- 40. M.M. Jaksic, Int. J. Hydrogen Energy, 12 (1987) 727.
- 41. C. Fan, D.L. Piron, A. Sleb, and P. Paradis, *J. Electrochem. Soc.*, 141-2 (1994) 382.
- 42. G. Lu, G. Zangari, Electrochim. Acta, 47 (2002) 2969.
- 43. W.T. Napporn, H. Laborde, J.-M. Léger, C. Lamy, *J. Electroanal. Chem.*, 404 (1996) 153.
- 44. I.G. Casella, T.R.I. Cataldi, A. Guerrieri, E. Desimoni, *Anal. Chim. Acta.*, 335 (1996) 217.
- 45. K. Bouzek, K.-M. Mangold, K. Juettner, *Electrochim. Acta*, 46 (2000) 661.
- 46. J. Sarrazin, M. Persin, M. Cretin, Macromol. Symp., 188-12 (2002).
- 47. V. Saxena, B.D. Malhotra, *Current Applied Physics*, 3 (2003) 293.
- 48. Southampton Electrochemistry Group, *Instrumental Methods in Electrochemistry*, Wiley, New York, 1985.
- 49. I. Arul Raj, Journal of Materials Science, 28-16 (1993) 4375.

- 50. N. Myung, Bull., Korean Chemical Society, 22 (2001) 994.
- 51. L.J. Gao, G.W. Anderson, P.R. Noton, Z. Lu, J.P. McCaffrey, M.J. Graham, *Can. Journal of Applied Physics*, 78 (1995) 5795.
- 52. B.A. Boukamp, *Equivalent Circuit Users Manuel Report* CT88/265/128, Department of Chemical Technology, University of Twente, The Nederlands, 1989.
- 53. M.R. Gennero de Chialvo, A.C. Chialvo, J. Electroanal. Chem., 448 (1998) 87.
- 54. S-I. Tanaka, N. Hirose, T. Tanaki, J. Electrochem. Soc., 146 (1999) 2477.
- 55. A. Kawashima, E. Akiyama, H. Habazaki, K. Hashimoto, Mater. Sci. Eng. A226-228 (1997) 905.
- 56. C. Cheung, F. Djuanda, U. Erb, G. Palumbo, Nanostruct. Mater., 5 (1995) 513.
- 57. M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, Pergamon Press, Oxford, 1966.
- 58. A. Rami, A. Lasia, J. Appl. Electrochem. 22 (1992) 376.
- 59. B. Borresen, G. Hagen, R. Tunold, *Electrochim. Acta*, 47 (2002) 1819.
- 60. E. Ndzebet, O. Savadogo, Int. J. Hydrogen Energy, 20 (1995) 635.
- 61. A. Krolikowski, A. Wiecko, *Electrochim. Acta*, 47 (2002) 2065.
- 62. L. Bai, L. Gao, and B.E. Conway, J. Chem. Soc. Faraday Trans., 82-2 (1993) 235.
- 63. J.G. Highfield, K. Oguro, B. Grushko, *Electrochim. Acta*, 47 (2001) 465.
- 64. C.A. Marozzi, A.C. Chialvo, *Electrochim. Acta*, 46 (2001) 861.
- 65. M.C. Taveres, S.A.S. Machado, L.H. Mazo, *Electrochim. Acta*, 46 (2001) 4359.
- 66. N. Krstajic, S. Trasatti, J. Appl. Electrochem., 28 (1998) 1291.
- 67. S.A.S. Machado, L.H. Mazo, *Electrochim. Acta*, 46 (2001) 4359.
- K.R. Christmann in 'Hydrogen Effects in Catalysis', Z. Paal, P. G. Menon eds., Chap 1, Marcel Dekker (1988).
- 69. A. Lasia, A. Rami, J. Electrochem. Soc., 294 (1990) 123.
- 70. R. Simpraga, B.E. Conway, *Electrochimica Acta*, 43 (1998) 3045.
- 71. S. Trasatti, O.A. Petrii, Pure App. Chem., 63 (1991) 711.
- 72. S. Omanovic, S.G. Roscoe, *Langmuir*, 15 (1999) 8315.
- 73. S. Omanovic, S.G. Roscoe, J. Colloid Interf. Sci., 227 (2000) 452.
- 74. J. Panek, A. Serek, A. Budniok, E. Rowinski, E. Lagiewka, *Int. J. Hydrogen Energy*, 28 (2003) 169.
- 75. L. Birry, A. Lasia, J. Appl. Electrochem., 34 (2004) 735.
- 76. P. Elumalai, H.N. Vasan, N. Munichandraiah, S.A. Shivashankar, *J. Appl. Electrochem.*, 32 (2002) 1005.

- 77. O. Savadogo, E. Ndzebet, Int. J. Hydrogen Energy, 26 (2001) 213.
- 78. R.D. Armstron, M. Henderson, J. Electroanal. Chem., 39 (1972) 81.
- 79. E.B. Castro, M.J. de Giz, E.R. Gonzalez, J.R. Vilche, *Electrochim. Acta*, 42 (1997) 951.
- 80. J.M. Jaksic, M.V. Vojnovic, N.V. Krstajic, *Electrochim. Acta*, 45 (2000) 4151.
- 81. F. Rosalbino, G. Borzone, E. Angelini, R. Raggio, *Electrochim. Acta*, 48 (2003) 3939.
- 82. M. Kramer, M. Tomkiewicz, J. Electrochem. Soc., 131 (1984) 1283.
- 83. H.S. Lin, Phys. Rev. Lett., 55 (1985) 529.
- 84. Z. Kerner, T. Pajkossy, Electrochim. Acta, 46 (2000) 207.
- 85. T. Pajkossy, J. Electroanal. Chem., 364 (1994) 111.
- 86. S. Omanovic, M. Metikos-Hukovic, Thin Solid Films, 226 (1995) 35.
- 87. L. Chen, A. Lasia, J. Electrochem. Soc., 139 (1992) 3214.
- 88. G. J. Brug, A. L. G. Van Der Eeden, M. Sluyters-Rehbach, J. H. Sluyters, J. *Electroanal. Chem.*, 176, 275 (1984).
- 89. C. Fan, D. L. Piron, M. Milleur, L.-P. Marin, Can. J. Chem. Eng., 71 (1993) 570.
- 90. M.M. Jaksic, Int. J. Hydrogen Energy, 26 (2001) 559.
- 91. M.M. Jaksic, C. M. Lacnjevac, B. N. Grgur, N. V. Krstajic, J. New Mat. Electrochem. Sys., 3 (2000) 169.
- 92. N.V. Krstajic, B.N. Grgur, N.S. Mładenovic, M.V. Vojnovic, M.M. Jaksic, *Electrochim. Acta*, 42 (1997) 323.
- P.K. Babu, H.S. Kim, A. Wieckowski, E. Oldfield, *J. Phys. Chem.*, B, 107 (2003) 7595.
- Y. Y. Tong, H. S. Kim, P.K. Babu, P. Waszczuk, A. Wieckowski, E. Oldfield, J. Am. Chem. Soc., 124 (2002) 468.; C. Vericat, M. Wakisaka, R. Haasch, P.S. Bagus, A. Wieckowski, J. Solid State Electrochem., in press,
- 95. Wieckowski, personal communication
- 96. P. Oelhafen, E. Hauser, H.J. Guntherodt, K.H. Bennemann, *Phys. Rev. Lett.*, 43 (1979) 1134.
- 97. P. Oelhafen, E. Hauser, H.J. Guntherodt, Solid State Commun. 35 (1980) 1017.
- 98. J. Kubler, K.H. Bennemann, R. Lapka, F. Rosel, P.Oelhafen, H.J. Guntherodt, *Phys. Rev.* B, 23 (1981) 5176.
- 99. A. Stephen, D. Kalpana, M.V. Ananth, V. Ravichandran, *Int. J. Hydrogen Energy*, 24 (1999) 1059.

- 100. Schlapka, M. Lischka, A. Gross, U. Kasberger, P. Jakob, *Physical Rev. Lett.*, 91(2003) paper 016101
- 101. J.R. Kitchin, J.K. Norskov, M.A. Barteau, J.G. Chen, *J. Chem. Phys.*, 120 (2004) 10240.
- 102. A. Zouaoui, O. Stephan, M Carrier, J.C. Moutet, *J. Electroanal. Chem.* 474 (1999) 113.
- 103. A. Leone, W. Marino, B.R. Scharifker, J. Electrochem. Soc., 139-2 (1992) 438.

LIST OF PUBLICATIONS AND CONFERENCE PRESENTATIONS

Publications in Peer Reviewed Journals

• E. Navarro-Flores, Z. Chong and S. Omanovic, Characterization of Ni, NiMo, NiW and NiFe Electroactive Coatings as Electrocatalysts for the Hydrogen Evolution in an Acidic Medium submitted to J.Molec.Catal.A: Chemical, in press

Conferences

- *INVITED:* E. Navarro Flores, Z. Chong, S. Omanovic, *Nickel/Conducting Polymers Electrocatalysts for Hydrogen Evolution*, 72e Congrés de l'ACFAS, Montreal, QC, Canada, 2004.
- *INVITED*: E. Navarro-Flores, S. Omanovic, *Nickel-based/Conducting Polymer Electrocatalysts for Hydrogen Evolution*, 87th Canadian Chemistry Conference and Exhibition, London, ON, Canada, 2004.
- E. Navarro Flores, Z. Chong, S. Omanovic, *Nickel/Conducting Polymers Electrocatalysts for Hydrogen Evolution in an Acidic Medium*, 18the Canadian Symposium on Catalysis, Montreal, QC, Canada, 2004.

APPENDIX A.

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η	Potential decay slope	C_{dl}	Areal	~ ~ ~					
(V)	(V s ⁻¹)	(F)	(cm ²)	0					
	Ni / PANI - 20 / 5								
-0.035	0.31	2.060E-05	1.03	6.04					
-0.055	0.52	2.533E-05	1.27	7.43					
-0.075	0.66	2.815E-05	1.41	8.25					
-0.095	0.78	3.114E-05	1.56	9.13					
-0.115	1.01	3.205E-05	1.60	9.40					
-0.135	1.25	3.357E-05	1.68	9.85					
-0.155	1.71	3.151E-05	1.58	9.24					
-0.175	2.52	2.844E-05	1.42	8.34					
-0.195	3.67	2.620E-05	1.31	7.68					
-0.215	5.56	2.374E-05	1.19	6.96					
-0.235	8.58	2.155E-05	1.08	6.32					
Ni / PPY - 20 / 5									
-0.065	0.251	2.467E-05	1.234	7.235					
-0.075	0.385	2.703E-05	1.352	7.928					
-0.095	0.633	2.952E-05	1.476	8.658					
-0.115	0.951	2.902E-05	1.451	8.509					
-0.135	1.303	2.855E-05	1.428	8.374					
-0.155	1.834	2.710E-05	1.355	7.947					
-0.175	2.594	2.552E-05	1.276	7.484					
-0.195	3.272	2.487E-05	1.244	7.294					
-0.215	4.584	2.332E-05	1.166	6.838					
0.255	9.089	1.969E-05	0.985	5.775					
	<u>Ni / Pl</u>	PY - Co - 20							
-0.115	0.029	4.427E-05	2.214	12.984					
-0.135	0.075	3.997E-05	1.999	11.723					
-0.155	0.129	3.879E-05	1.939	11.375					
-0.175	0.197	3.813E-05	1.907	11.183					
-0.195	0.294	3.736E-05	1.868	10.956					
-0.215	0.431	3.667E-05	1.834	10.754					
-0.235	0.629	3.592E-05	1.796	10.534					
-0.255	0.916	3.482E-05	1.741	10.211					
-0.275	1.332	3.362E-05	1.681	9.860					
-0.295	1.905	3.259E-05	1.630	9.558					
-0.315	2.746	3.109E-05	1.555	9.119					

 Table A.1
 Potential relaxation data and calculated parameters for the Ni / CP

 electrocatalysts under study.

η	R _{el}	CPE1	<u> </u>	R ₁	CPE ₂	n.	R ₂	C _{dl}		
(V)	(Ω)	(F s ⁿ⁻¹)	111	(Ω)	(F s ⁿ⁻¹)	112	(Ω)	(F)		
	Ni / PANI - 20 / 5									
-0.135	6.43	7.65E-05	0.88	1728.43	-	-	-	2.72E-05		
-0.335	5.52	7.86E-05	0.87	87.61	-	-	-	2.51E-05		
Ni / PPY - 20 / 5										
-0.095	5.57	7.42E-05	0.90	3402.71	9.43E-04	0.61	5.26	3.19E-05		
-0.135	5.68	7.31E-05	0.91	2427.71	9.50E-04	0.62	5.16	3.28E-05		
-0.260	5.49	7.09E-05	0.91	463.80	1.56E-03	0.56	6.21	3.30E-05		
Ni / PPY - Co - 20										
-0.135	21.52	4.67E-04	0.56	66.61	5.52E-05	0.89	12811.14	2.86E-05		
-0.175	19.23	5.31E-04	0.53	83.60	5.26E-05	0.89	7597.13	2.82E-05		
-0.260	16.49	6.82E-04	0.49	102.88	5.41E-05	0.89	2051.77	2.94E-05		

Table A.2 EEC parameters obtained by fitting EIS experimental spectra recorded at various overpotentials on the investigated Ni /CP / GC electrocatalytic coatings using the EEC models presented in Figure 5.6.