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Studies on Pulse Electrodeposition of Pt-Ni binary Alloy For **Electrochemical Cell Applications**

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Abstract. The possibility to prepare a Pt-Ni bimetallic catalyst for electrochemical cells applications using a two-step electrochemical process was tested. The binary alloy catalyst was deposited on a graphitic substrate covered with carbon nanofibers previously treated in oxygen plasma. This support system provides a high surface area for the alloy particles, improving considerably the catalytic activity. A simultaneous reduction reaction of Pt and Ni was performed by strictly controlling the metals ratios in the solution and by choosing suitable deposition parameters. A pulsed current technique was applied. Varying the Pt: Ni ratio in the electrolyte and adjusting the deposition main parameters lead to a homogeneous distribution of the catalyst. A comparison with pure platinum nano-scaled supported electrodes is also presented, regarding hydrogen/oxygen evolution reaction. Although a significant decrease of platinum amount was achieved by alloying, a higher activity of the catalyst was obtained. Morphology, structure, and chemical composition of the catalysts was investigated by means of scanning electron microscopy combined with energy dispersive X-ray spectroscopy. X-ray diffraction was used to identify the alloy phase composition. The amount of deposited alloy determined using thermogravimetric measurements correlated with the cyclic voltammetry performed in 0.5 M H₂SO₄ solution to estimate the electrochemical surface area offered important information regarding the catalytic activity.

1. Introduction

The most common catalyst material for both fuel cells and electrolysers is platinum. Improving the efficiency of platinum-based catalysts for the main electrochemical reactions, such as oxygen reduction/oxidation reaction, has always been a priority for research and development [1]. As this material is a very scarce metal, numerous studies have been conducted to reduce the platinum consumption, while maintaining the essential characteristics. Alloying has been demonstrated to be a suitable approach to obtain advanced catalytic materials [2]. Recently, platinum alloys have attracted attention due to their great electrocatalytic properties and applicability in various fields, ranging from catalytic applications in fuel cells, electrolysers, batteries, and sensors to medical and aerospace industry. Lately, Pt-based binary and ternary alloys have been developed using various routes, in order to achieve a better control of particle size and phase composition, aspects which are considered significant for an optimum catalyst [3]. Among the various deposition methods, electrodeposition exhibits several distinctive and unique characteristics [4]. Electrodeposition is an appropriate method for catalyst synthesis because it is both easy to apply and requires a low-cost technology. Moreover,

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using this technique, a good control of the catalyst properties can be achieved [5]. By reducing the catalyst particle size, an increase in the active surface area is attained, and moreover, a significant decrease in the Pt loading may be reached, correlated with faster reaction rates. Alloying Pt with non-noble metals like Ni or Co reduces the Pt content of the electrocatalysts and significantly increases the electrochemical activity [6]. Likewise, the addition of a second metal has been shown to improve the surface chemistry and the reactivity of Pt and confers the catalyst a bi-functional mechanism [2, 7].

Particularly, Pt-transition metal (Pt-M) bimetallic alloys, such as Pt–Co, Pt–Ni, Pt–Fe, Pt–Cr, and Pt–Ti were found to exhibit a lower overpotential for the oxygen reduction reaction, presenting a higher catalytic activity [8-10]. Pt₃Ni alloy phase composition was found to enhance the ORR activity by two orders of magnitude (in comparison to Pt/C catalysts) by changing the electronic structure of Pt surface atoms [8]. Furthermore, Ni alloyed with Pt was found to reduce the electronic binding energy of Pt, which also contributes to a higher activity of the catalyst [2].

In addition, an appropriate support material for the catalyst particles, with a great surface area, high electrical conductivity, and stability, offers a good dispersion of Pt and Pt alloy nanoparticles, reaching a maximum utilization degree of the noble material. Carbon based materials with delocalized π -electrons, are considered to be an excellent support for the catalyst particles, due to the extremely large surface area, high electrical conductivity, good mechanical resistance and chemical and thermal stability [2, 11].

Considering the advantages of electrodeposition, such as high purity of deposits and relatively simple procedure of deposition, in the present study, platinum–nickel (Pt-Ni) bimetallic alloy nanoparticles with a uniform mean diameter of 10 nm, were anchored onto a carbon support material using the electrodeposition method. The resulting Pt-Ni/CNF catalysts have been characterized by Scanning Electron Microscopy (SEM), X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX). The electrocatalytic properties of the Pt-Ni/CNF electrodes have been investigated by cyclic voltammetry (CV).

2. Experimental

2.1 Materials and methods

Graphene related materials (GAqUA, carbon nanofibers-water suspension) with high specific surface area and good electrical conductivity purchased from Grupo Antolin Ingineria, Spain were used as support material for the catalyst alloy particles. CNF are firstly deposited on the surface of a commercially available gas diffusion layer (GDL, H2315 I2C8, Freudenberg FCCT SE & Co. KG) by air brushing (USI Prism BT 500 System), having a uniform 10 μ g cm⁻² CNF loading. Other reagents used for the Pt-Ni alloy deposition are hexachloroplatinic acid (H₂PtCl₆) (Galvatron Platinbad, 10 g Pt L⁻¹, Wieland Edelmetalle GmbH, Germany), nickel (II) chloride hexahydrate (97%-Ni, Merck KGaA, Darmstadt, Germany), sulfuric acid (H₂SO₄) (98%, Carl Roth GmbH + Co. KG, Germany) and distilled water. Three electrodeposition baths were prepared, with different concentrations of nickel, as presented in table 1.

Table 1.	Chemical	composition	of PtNi	deposition	baths

Bath	1:2	1:4	1:6
Pt content [g L ⁻¹]	10	10	10
Ni content [g L ⁻¹]	20	40	60

The main challenge of the catalyst nanoparticles electrodeposition on this specific support material is the hydrophobic character of the carbon. For a homogenous and fine dispersed deposition of the catalyst, a functionalization treatment of the substrate surface is advantageous. An oxygen plasma treatment of the carbon surface before the electrodeposition significantly improves the catalyst distribution. The detailed procedure and parameters are described elsewhere [7,12]. Moreover, the effects of the electrolyte composition and electrodeposition parameters have been investigated in detail. For electrocatalytic applications, nucleation step should be predominant in order to generate numerous particles and consequently a large electrochemical active surface area. Various techniques, including CV, SEM, XRD were used in this study to investigate the catalytically relevant parameters of the developed electrodes. The morphology, size and distribution of catalyst particles on the CNF support were examined by SEM. XRD method was used to investigate the phase structure of the developed catalyst materials and further to calculate the crystallite size according to Debbie-Scherrer equation.

2.2 Electrode preparation

The synthesis process of Pt–Ni electrodes using electrodeposition consisted of two steps. The first step was the surface modification of the carbon support material, creating a hydrophilic layer with functional groups attached onto the surface of the CNF. The second step was the galvanostatic electrodeposition of Pt–Ni and Pt on the pretreated carbon substrates.

As the first step was developed and described in a previous work, the focus was directed on the second step, namely the Pt–Ni co-deposition. The electrodeposition was performed in a 250 ml plating bath containing 10 g L⁻¹ M H₂PtCl₆ and 20-60 g L⁻¹ M NiCl₂ · 6 H₂O, in a three-electrode system, consisting of working electrode (as-prepared carbon support), counter electrode (platinum disk), and reference electrode-saturated calomel electrode (SCE), using an electrochemical workstation (Potentiostat/Galvanostat Ivium Technologies Vertex). The active area of the working electrode was 1 cm². Deposition parameters such as current density, applied time (t_{on} and t_{off}), and electrolyte composition were varied in order to obtain an optimum electrochemical performance of Pt–Ni alloy catalysts. Moreover, a good dispersion of the catalyst on the carbon support is an important condition for attaining a superior electrocatalytic activity for fuel cells reactions.

3. Results and Discussions

3.1 Influence of the deposition current density

The influence of the applied current density on morphology and chemical composition of the Pt-Ni alloy has been investigated by applying different current densities in the range of 50 to 200 mA cm⁻². The finest structures were obtained for three of the applied values, namely 100 mA cm⁻², 125 mA cm⁻², 150 mA cm⁻² according to the SEM micrographs presented in figure 1.



Figure 1. SEM micrographs of PtNi/CNF samples deposited with: a) 100 mA cm⁻²; b) 125 mA cm⁻²; c) 150 mA cm⁻² from electrolyte 1:2, with $t_{on} = 12$ ms, d.c = 10%, 2000 cycles.

The other variables like bath composition, $t_{on} = 12$ ms, d.c = 10%, and number of cycles (2000) were maintained constant. As the current density affects the nucleation process of the catalyst particles, an increase in the current density over 125 mA cm⁻² intensifies the hydrogen evolution reaction (HER), favouring the particles growth mechanism by achieving the diffusion limiting current density. According to the preliminary linear voltammetry performed with the working electrolyte, the electrodeposition of Pt-Ni alloy using a current density higher than 125 mA cm⁻² takes place under mass transfer limitations for platinum and the excess current density is used for the nickel deposition, simultaneously with HER. As HER proceeds with a faster rate than nickel deposition, a larger fraction of the excess current is used towards the proton reduction reaction and consequently the CNF layer may be damaged. As it can be observed in SEM micrographs illustrated in figure 1, when a higher current density is applied, the particles start to grow, and dendrites start to form. An optimum nucleation and size particle is obtained for a deposition conducted with 125 mA cm⁻². Furthermore, the SEM investigation are correlated with the cyclic voltammetry measurements performed in 0.5 M H₂SO₄ solution, in order to highlight the electrochemical activity of the catalysts. The electrodes were scanned for 200 cycles with 100 mV s⁻¹ scan rate and the results showed in figure 2 represent the last scan of each sample.



Figure 2. CV polarization curves for three PtNi/CNF electrodes deposited with different current densities (100 mA cm⁻², 125 mA cm⁻² and 150 mA cm⁻²) in 0.5 M H₂SO₄ solution with a scan rate of 100 mV s⁻².

CV plots performed on the three investigated samples exhibit, as expected, the same shape as for a typically pure platinum electrode. In the potential range of -0.2 - 0.1 V vs. SCE, the peaks are associated to the adsorption/desorption processes of hydrogen on Pt-Ni surface. In the anodic branch, in the potential range of 0.1 - 0.6 V vs. SCE, the curve corresponds to the charge of the double layer due to the oxygenated groups on the carbon support surface [9]. Starting from 0.6 V vs SCE, the oxidation process of Pt takes place. In the cathodic polarisation, the correspondent reduction peak from 0.5 V is linked to the reduction process of platinum oxides previously formed. In the presented voltammograms, the higher activity is observed for the Pt-Ni sample deposited with 125 mA cm⁻² and this aspect may be attributed to the amount of catalyst and size of the particles in the alloy [9].

3.2 Influence of the ton and toff

By changing the main deposition parameters, it is possible to modify the alloy composition, current efficiency and nucleation rate [13]. Regarding the deposition time, generally, a short t_{on} pulse makes the electrodeposition to be dominated by nucleation. The t_{off} pulse has also a significant role in the deposition kinetics since many effects like replenishment of concentration gradients and recrystallisation occur in this step. The plots presented in figure 3 display the influence of t_{on} on the ECSA of the catalysts. A higher value is obtained for the sample deposited with 12 ms (16 m² g⁻¹ Pt).

The effect of t_{off} pulse on the nucleation rate is less substantial. If the deposition current density is maintained for a longer period of time, the deposition is under high crystal growth conditions, the diffusion layer is depleted in the platinum ions, generating a concentration gradient between the bulk electrolyte and the electrolyte/electrode interface and the electrodeposition changes to diffusion limited

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step [13]. Co-deposition of Pt with Ni can be achieved only under diffusion limiting conditions for Pt, resulting also in hydrogen evolution [4]. Consequently, the deposition of nickel, which is less noble than platinum takes place easier in these specific conditions. In the case of smaller t_{on} (less than 5 ms), the deposition consists predominantly of platinum particles. When a higher t_{on} is applied, nickel particles are co- deposited forming the alloy structure. A further increase of t_{on} (more than 15 ms) leads to a decrease in the nucleation rate and the system is controlled by the crystal growth and the alloy particles start to increase. Figure 4 presents the structure of the catalytic PtNi material obtained with 12 ms pulse time.

3.3 Influence of the number of cycles

Number of cycles has a strong influence on the catalyst loading of the electrodes. Since the total deposition time is higher, according to Faraday's Law, the amount of the alloy is correspondingly higher. TGA measurements confirm the increase in the amount of the metallic catalyst, proportional with the applied number of cycles. Regarding the morphology and the chemical composition, no structural changes can be observed when increasing the number of applied cycles. The size of the particles remains constant according to XRD measurements.



Figure 3. CV polarization curves for three PtNi/CNF electrodes deposited with different t_{on} (3 ms, 6 ms, 12 ms), 125 mA cm⁻², in 0.5 M H₂SO₄ solution with a scan rate of 100 mV s⁻².



Figure 4. SEM micrographs of PtNi/CNF samples deposited with 12 ms; from electrolyte no. 1, with a current density of 125 mA cm-2, constant d.c of 10%, and 2000 cycles (mag. 50000x).

3.4 Influence of the bath concentration

The chemical composition of the working electrolyte has been shown to influence the alloy phase composition of the catalyst particles. Different ratios of Ni could be co-deposited with Pt by keeping the concentration of H_2PtCl_6 constant (10 g L⁻¹) and varying that of NiCl₂ in the plating bath (from 20 g L⁻¹ to 60 g L⁻¹). As XRD measurements confirm, increasing the Ni ions concentration in the deposition bath determines an increase in the Ni content found in the catalyst alloy structure, correlated with a higher amount of NiPt3 alloy phase. Moreover, a higher concentration of nickel in the electrolyte determines an increase in the nucleation rate and additionally, creates changes in the catalyst structure. The deposition is acicular when higher Ni concentration is applied. Consequently, smaller particle sizes are obtained for Pt-Ni alloys deposited from the deposition bath with a higher nickel concentration (figure 5).



Figure 5. SEM micrographs of PtNi/CNF samples deposited from different Ni content deposition baths a) 1:2; b) 1:4; c) 1:6, with 125 mA cm⁻², $t_{on} = 12$ ms, constant d.c of 10%, 2000 cycles.

In figure 6, the CV measurements for three PtNi/CNF electrodes deposited from different deposition baths (1:2, 1:4, 1:6), with 125 mA cm⁻², in 0.5 M H_2SO_4 solution with a scan rate of 100 mV s⁻² are presented.

Figure 7 shows the XRD patterns of the Pt/CNF and PtNi/CNF electrodes with different nickel contents. The intensity of Pt characteristic peaks such as Pt (111), Pt (200), Pt (220), and Pt (311) decreases when the Ni content increases in the deposition bath. Moreover, all the detected peaks for PtNi samples are shifted toward higher values of 2θ angle in comparison to standard spectra of Pt.

During the co-deposition process, nickel atoms randomly substitute platinum atom positions in the metallic lattice. As it can be remarked from the diffractograms, no characteristic lines for pure Ni can be observed [14]. As Ni atoms are considerably smaller that platinum atoms, lattice parameters become also smaller, fact which clearly emphasizes the metallic bond between Pt and Ni. The crystallite size is calculated from the Pt_3Ni (111) reflexion using Scherrer Equation.



Figure 6. CV polarization curves for three PtNi/CNF electrodes deposited from different deposition baths (1:2, 1:4, 1:6), with 125 mA cm⁻², in 0.5 M H₂SO₄ solution with a scan rate of 100 mV s⁻².



Figure 7. XRD patterns for Pt/CNF (reference electrode) and PtNi/CNF electrodes deposited from different bath compositions (1:2, 1:4, 1:6)

3.5. HER/OER on the PtNi/CNF developed electrodes

As it can be observed in figure 8, HER is significantly intensified and the onset potential decreases considerably for PtNi/CNF samples in comparison to a reference Pt/CNF electrode.

The HER depolarisation observed in the linear voltammetric plots is influenced by the presence of nickel in the structure of the catalyst. Beyond the HER onset potential, the cathodic current densities are considerably higher for PtNi/CNF electrodes at the same overpotential value. Around -0.5 V vs. SCE, the cathodic current density for PtNi/CNF (2000 cycles) reaches significantly higher current densities (400 mA cm⁻²) in comparison to the reference Pt/CNF sample. The enhanced HER activity can be attributed mainly to the increased ECSA.

OER for platinum containing electrodes is known to be slow in acidic medium due to catalyst surface oxidation and Ni lower stability. Although the Pt/CNF shows a sluggish OER process (figure 9) with an onset potential around 1.5 V vs. SCE, the PtNi/CNF electrode prepared with 2000 cycles exhibits a lower onset potential of around 1.4 V vs. SCE, developing higher current densities in comparison to Pt/CNF sample at the same overpotential.



Figure 8. HER on selected Pt/CNF and PtNi/CNF electrodes in 0.5 M H_2SO_4 solution, acquired with a polarization rate of 5 mV s⁻¹



Figure 9. OER on selected Pt/CNF and PtNi/CNF electrodes in 0.5 M H_2SO_4 solution, acquired with a polarization rate of 5 mV s⁻¹

4. Conclusions

Pt-based alloys are considered a promising alternative to pure platinum catalyst for HOR/ORR in fuel cells or HER/OER in electrolysers, due to their low Pt loading and high activity. The present work suggests a new route of electrodepositing Pt-Ni alloy nanoparticles on CNF, using a two-step deposition process. The influence of the most important deposition parameters like current density, time and bath composition were studied in order to obtain PtNi catalysts with high electrochemical activity, which perform well in electrochemical systems. Improved results were obtained applying 125 mA cm⁻² current density for 12 ms (2000 cycles), from the PtNi 1:4 electrolyte. The SEM micrographs are in good agreement with CV measurements as well as with TG and XRD investigations. XRD analysis confirms Pt₃Ni alloy phase formation on the CNF structure, since the Pt characteristic peaks as identified by the diffraction patterns shift from that of pure Pt.

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