

## Development of Ni-Mo, Ni-W and Ni-Co Macroporous Materials for Hydrogen Evolution Reaction

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The hydrogen evolution reaction (HER) is the cathodic process in many important electrochemical technologies. According to the Brewer intermetallic bonding theory, molybdenum and tungsten were alloyed with nickel (hypo-hyper-d- electronic transition metal) in order to increase the intrinsic catalytic activity for HER. Cobalt was also combined with nickel to evaluate the effect of this metal in the intrinsic catalytic activity. In all the cases, electrodeposition at very high current densities provided macroporous materials of quasy-cylindrical pores due to the fact that the metallic deposition takes place simultaneously to the gas bubbling at high current densities.

Morphology of the developed electrodes was characterized by confocal laser scanning microscopy, and HER on these electrodes was evaluated in 30 wt.% KOH solution by means of steady-state polarization curves and electrochemical impedance spectroscopy (EIS). Results show that the developed materials manifest higher apparent catalytic activity than that reported for a smooth commercial polycrystalline nickel electrode.

### 1. Introduction

The hydrogen evolution reaction (HER) is one of the most studied electrochemical reactions because it is the main reaction in many important electrochemical technologies, such as alkaline water electrolysis and chlor-alkali production. However, the high overpotentials for HER hinder the high scale hydrogen production by means of alkaline water electrolysis, the most promising method for the hydrogen production from renewable energy sources (Miltner et al., 2009). Concerning to the HER mechanism, it is widely accepted that it occurs via two steps; HER starts with a proton discharge to give adsorbed hydrogen atom (Volmer reaction, (1)):



Followed by recombination of two adsorbed H atoms (Tafel reaction, (2)) or an electrodesorption step (Heyrovsky reaction, (3)) yielding H<sub>2</sub>.



The optimum electrode materials for HER must combine strong intrinsic catalytic activity, large surface area, stability of performance and low cost. Platinum shows the highest activity for HER but his cost is too high. For this reason, there are many researches to find novel materials with high intrinsic activity for HER to replace the use of noble metals and to diminish the cost. Many transition metal alloys have been characterized as hydrogen electrodes in water electrolysis. Most alloys are nickel-based binary or ternary codeposits. Binary or ternary catalytic systems often show improved catalytic activity, attributed to

synergism, modification of electronic properties or geometric. Metals of the left half of the transition series in the periodic table with empty or less-filled d-orbitals, such as tungsten, molybdenum, lanthanum, hafnium, zirconium, etc., are alloyed with metals of the right half of the series with more filled d-bands, such as iron, cobalt, and nickel; a maximum in bond strength and stability of the intermetallic alloy phases is expected, and there is a well-pronounced synergism in the electrocatalysis. This condition implies that some of the electrons of the metal with more filled d-bands are shared with the metal with less-filled or empty d-orbitals. This synergetic effect often exceeds the effects of the individual parent metals and approaches reversible behaviour within a wide range of current density (Brewer, 1963).

On the other hand, it has been demonstrated that alloying Ni with Co can improve the intrinsic catalytic activity as a consequence of the synergism among the catalytic properties of nickel (low hydrogen overpotential) and of cobalt (high hydrogen adsorption) (Lupi et al., 2009).

The aim of the present work is the development of Ni-Mo, Ni-W and Ni-Co macroporous electrodes in order to evaluate their suitability for the HER in terms of catalytic activity. The developed electrodes were characterized morphologically by confocal laser scanning microscopy, and electrochemically in 30 wt.% KOH solution by means of steady-state polarization curves and electrochemical impedance spectroscopy (EIS).

## 2. Experimental

### 2.1 Preparation of electrodes

The metallic coatings were deposited onto AISI 304 stainless steel disc electrodes (0.5 cm<sup>2</sup> geometric area). These substrate materials were set up with the pre-treatment process described in our previous work (Herraiz-Cardona et al., 2012), as an initial step.

Electrodes were galvanostatically co-deposited at high current density. According to Brenner (1963), certain elements, such as Mo and W, can not be electrodeposited from aqueous solution but they can be codeposited easily with iron group metals such as Ni, forming an alloy. With respect to Ni-Co codeposition, it is classified as an anomalous codeposition, the thermodynamically less noble metal (Co) deposits preferentially from baths containing different metallic ions. Table 1 summarizes the bath compositions and the experimental conditions used in the synthesis of the electrodes. For the codeposition of Ni with Mo, W and Co, the corresponding salt was diluted in the minimum distilled water volume (ca. 1 mL) and injected to the electrodeposition bath 45 min later of the beginning of the electrodeposition process to avoid the preferential deposition. According to the Faraday's law, 15 min is the time necessary to carry out the complete Co, Mo and W electrodeposition.

Electrodepositions were carried out in a thermostated one-compartment cell with the substrate surface to be coated in horizontal "face-up" position, allowing the free release of the generated gas bubbles. The solution inside the cell had a volume of 50 mL. A three-electrode configuration was employed for the electrodeposition process. A large-area platinum electrode was used as a counter electrode and a commercially available silver-silver chloride (Ag-AgCl) electrode with 3 M KCl solution was used as reference. The experiments were carried out by using an AUTOLAB PGSTAT302N potentiostat/galvanostat.

The surface morphologies of the electrocatalytic coatings obtained were studied by means of an OLIMPUS LEXT OLS3100-USS confocal laser scanning microscope.

*Table 1: Bath compositions and operating conditions used in the electrodeposition of the electrocatalytic coatings*

Electrode	Bath composition (g L <sup>-1</sup> )		Operating conditions	
Ni	NiCl <sub>2</sub> ·6(H <sub>2</sub> O)	48	Temperature (°C)	25
	NH <sub>4</sub> Cl	170		
NiCo	NiCl <sub>2</sub> ·6(H <sub>2</sub> O)	48	Current density (A cm <sup>-2</sup> )	1000
	NH <sub>4</sub> Cl	170		
	CoCl <sub>2</sub> ·6(H <sub>2</sub> O)	8		
NiMo	NiCl <sub>2</sub> ·6(H <sub>2</sub> O)	48	Time (min)	60
	NH <sub>4</sub> Cl	170		
	Na <sub>2</sub> MoO <sub>4</sub> ·2(H <sub>2</sub> O)	8		
NiW	NiCl <sub>2</sub> ·6(H <sub>2</sub> O)	48	pH	4.5
	NH <sub>4</sub> Cl	170		
	Na <sub>2</sub> WO <sub>4</sub> ·2(H <sub>2</sub> O)	13		

## 2.2 Electrochemical measurements

The catalytic activity for the HER on the synthesized electrocatalysts was determined by means of pseudo-steady-state polarization curves and electrochemical impedance spectroscopy (EIS). All these tests were performed in oxygen free 30 wt.% KOH solutions, obtained by bubbling N<sub>2</sub> for 15 min before the tests.

Polarization curves were potentiodynamically recorded from -1.60 V vs Ag/AgCl (-1.40 V vs SHE) up to the equilibrium potential, at a scan rate of 1 mV s<sup>-1</sup>, and at different temperatures: 30, 40, 50, 60, 70 and 80 °C. Before the tests, the working electrode was held at -1.60 V vs Ag/AgCl (-1.40 V vs SHE) in the same solution, in order to reduce the oxide film existing on the porous surface electrode layer, for the time needed to set up reproducible diagrams.

EIS measurements were recorded after obtaining the polarization curves. Alternating current impedance measurements were carried out at different temperatures (30, 50, and 80 °C), and at different cathodic overpotentials. The measurements were made in the frequency range of 10 kHz to 3 mHz. Ten frequencies per decade were scanned using a sinusoidal signal of 10 mV peak-to-peak. The complex nonlinear least square (CNLS) fitting of the impedance data was carried out with the Zview 3.0 software package.

The electrochemical measurements were carried out in the electrochemical cell developed by the Dpto. Ingeniería Química y Nuclear of the Universitat Politècnica de València (García-Antón et al., 2000). The developed electrode was used as the working electrode, placing the electrode/electrolyte interface on a vertical plane, in order to allow the free evolution of the produced hydrogen bubbles when necessary. The counter-electrode was a large-area Ni foam (INCOFOAM™), and the reference electrode was the Ag-AgCl electrode. All the electrochemical measurements were obtained by using an AUTOLAB PGSTAT302N potentiostat/galvanostat.

## 3. Results and discussion

Figure 1 shows confocal laser micrographs of the developed coatings. The superficial morphology of electrodes consists of a continuous matrix with cavities and pores distributed in the whole surface. The macroporosity of the layers is originated by the random nucleation of the dissolved hydrogen, which produces bubbles attached to the electrode surface, as a consequence of the high current density applied. The electrodeposition process takes place in the free area, and cavities are produced, where hydrogen generation in the neighbourhood continues draining (Marozzi and Chialvo, 2000). As can be observed from Figure 1, all the developed electrodes have a similar macrostructure but Ni-Mo and Ni-W electrodes have higher pore density, manifesting the later a rougher microstructure.

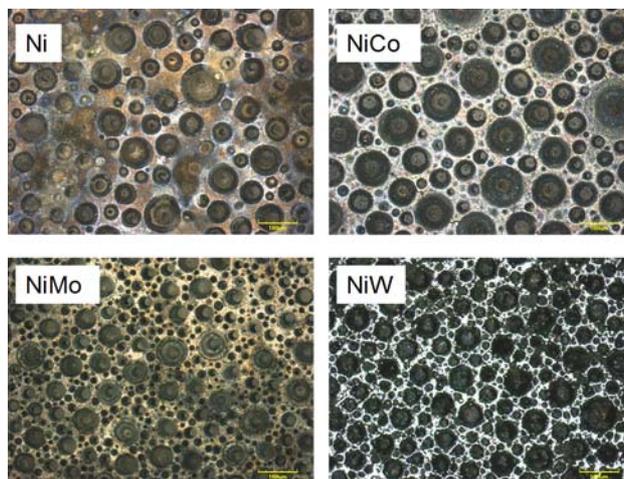


Figure 1: Confocal laser scanning micrographs of the developed electrocatalytic coatings

In order to investigate the catalytic activity for the HER on the developed electrocatalytic coatings, Tafel linear polarization measurements were performed in 30 wt.% KOH solutions. Figure 2.a shows Tafel curves recorded at two different temperatures: 30 °C (filled dots) and 80 °C (empty dots) on the synthesized electrodes. The curves performed on commercial smooth Ni electrode were also included to compare the obtained results. The curves were corrected with respect to the reversible HER potential at the given conditions and for the jR-drop. The corresponding electrochemical parameters (Tafel slope,

exchange current density, transfer coefficient) were obtained by means of the fitting by a linear regression and they are presented in Table 2. As can be observed from Figure 2.a and Table 2, all the developed electrodes present a single value for the Tafel slope between -0.08 and -0.18 V, this fact indicates that the HER on these electrodes is a purely kinetically controlled reaction described by the Tafel equation. According to the literature of HER on transition metals and the kinetic parameters shown in Table 2,  $b$  ranging from 80 to 120 mV dec<sup>-1</sup> at 30 and 80 °C, respectively, and  $\alpha$  close to 0.5 for all the coatings, HER proceeds via the same Volmer-Heyrovsky mechanism. In the Ni-Mo and Ni-Co electrodes higher values of the Tafel slope were obtained, this fact is related to the presence of oxides films on the catalyst surface (Navarro-Flores et al., 2005). The overpotential values at a fixed current density of -100 mA cm<sup>-2</sup>,  $\eta_{100}$ , were reported in Table 2 and plotted as a function of the temperature in Figure 2.b. This parameter would give an indication on the amount of energy (overpotential) that has to be invested to produce a fixed amount of hydrogen through the Faraday's law. The higher the operating temperature the lower the  $|\eta_{100}|$  is, as a consequence of an intrinsic catalytic activity improvement. From Figure 2 it is easily shown the better catalytic behaviour of the developed catalysts with respect to the smooth Ni electrode. As derived from both Table 2 and Figure 2, the the lowest  $|\eta_{100}|$  values are obtained for NiMo cathode, indicating that this electrode is the best overall catalysts.

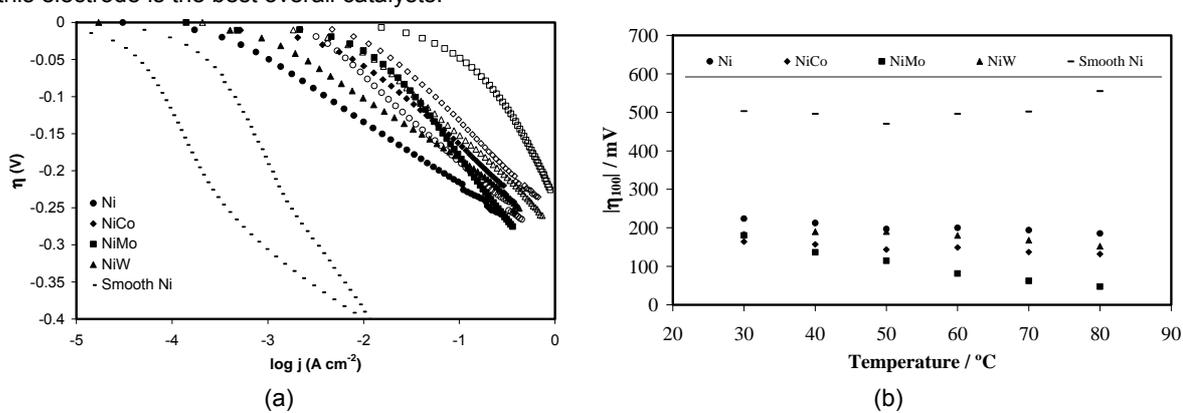


Figure 2: (a) Linear Tafel polarization curves recorded on the investigated electrocatalytic coatings in 30 wt.% KOH solution at 30 °C (filled dots) and at 80 °C (empty dots); (b) overpotentials at a current density of -100 mA cm<sup>-2</sup>,  $\eta_{100}$ , recorded on the investigated electrocatalytic coatings in 30 wt.% KOH solution

Table 2: Kinetic parameters of the HER obtained from the polarization curves recorded in 30 wt.% KOH solution at different temperatures

Catalyst	Temperature						Catalyst	Temperature					
	30	40	50	60	70	80		30	40	50	60	70	80
Ni							NiMo						
$b$ (mV dec <sup>-1</sup> )	91.3	88.9	91.4	97.2	105.8	114.2	$b$ (mV dec <sup>-1</sup> )	155.5	169.6	171.1	170.7	163.6	152.1
$i_0$ (mA cm <sup>-2</sup> )	0.33	0.41	0.68	0.86	1.46	2.34	$i_0$ (mA cm <sup>-2</sup> )	7.51	15.61	20.21	33.00	43.71	55.24
$\alpha$	0.66	0.70	0.70	0.68	0.64	0.61	$\alpha$	0.39	0.37	0.37	0.39	0.42	0.46
$\eta_{100}$	224	213	197	200	194	185	$\eta_{100}$	180.5	136.5	114.6	81.4	62.3	47.4
NiCo							NiW						
$b$ (mV dec <sup>-1</sup> )	117.7	120.9	125.2	127.0	130.4	135.6	$b$ (mV dec <sup>-1</sup> )	83.0	96.0	100.4	106.3	115.0	116.5
$i_0$ (mA cm <sup>-2</sup> )	3.91	4.89	6.86	6.95	8.73	10.52	$i_0$ (mA cm <sup>-2</sup> )	0.60	0.97	1.23	1.94	2.91	2.83
$\alpha$	0.51	0.51	0.51	0.52	0.52	0.52	$\alpha$	0.72	0.65	0.64	0.62	0.59	0.60
$\eta_{100}$	166	159	146	147	138	133	$\eta_{100}$	183.4	189.9	190.0	180.1	168.0	152.1

As it was expected, the same conclusion can be obtained from the study of the exchange current densities,  $j_0$ . The highest  $j_0$  values were obtained for Ni-Mo electrode, as a consequence of its better catalytic activity. The exchange current densities values of the studied cathodes increase with temperature. This increase is linear in a semi-logarithmic plot (Figure 3), which is in accordance with the Arrhenius law (Savadogo, 2001):

$$\log j = A' - \frac{E_a}{2.303 \cdot R} \cdot \frac{1}{T} \quad (4)$$

where  $E_a$  ( $\text{J mol}^{-1}$ ) represents the apparent activation energy for the HER, and  $A_0$  ( $\text{A cm}^{-2}$ ) is the pre-exponential factor. The intrinsic catalytic activity of an electrode in a given electrolyte is usually evaluated by means of the  $E_a$  value. The lower the  $E_a$ , the lower the energy requirements for hydrogen production. In Figure 3 has been included the regression lines obtained for the investigated electrocatalytic coatings. The  $E_a$  value has been calculated from the slopes. The lowest slope has been obtained for the Ni-Co electrocatalyst, thus this electrode has the lowest  $E_a$  value ( $17.1 \text{ kJ mol}^{-1}$ ) and, as a consequence, is the electrode with the better intrinsic catalytic activity. With respect to Ni-Mo and Ni-W electrodes, the calculated  $E_a$  values were  $34.7$  and  $37.5 \text{ kJ mol}^{-1}$  respectively, slightly lower than the  $E_a$  for Ni electrode ( $38.1 \text{ kJ mol}^{-1}$ ).

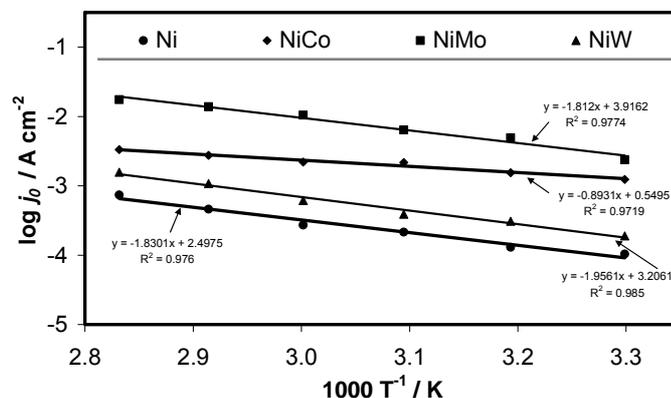


Figure 3. Electrochemical Arrhenius plot of the exchange current density at the reversible potential for the HER on the investigated electrocatalytic coatings in 30 wt.% KOH solution.

Figure 4 shows examples of EIS spectra recorded on the developed Ni electrocatalysts. The complex plane representation of the impedance data obtained reveals the presence of a straight line close to  $45^\circ$  at high frequencies followed by two strongly overlapped semicircles (that is two time constants). The same shape of the impedance curves was observed for the rest of investigated electrodes. The behaviour reported at high frequencies, independent of both temperature and overpotential, indicates a cylindrical pore geometry of finite length pores, as it was observed from the SEM study, with no mass transfer effects (De Levie, 1967). From Figure 4 it is shown that, as the cathodic overpotential increases the diameter of the two semicircles observed in the complex plane plot decreases for all the studied coatings. The increase in temperature reported the same behaviour. This phenomenon indicates that both semicircles (i.e. both time constants) are associated to the HER kinetics. In all the cases, at the highest cathodic overpotentials applied, where the vigorous gas bubbling causes too much interference, only one deformed semicircle appears. The studied cathodes characterized in the impedance complex plane plot by two semicircles dependents were modelled by using the two time constant parallel (2TP) EEC model. For the highest potentials, which only appear the one semicircle, one-time constant (1T) electric equivalent circuit (EEC) model was used to fit the impedance experimental data.

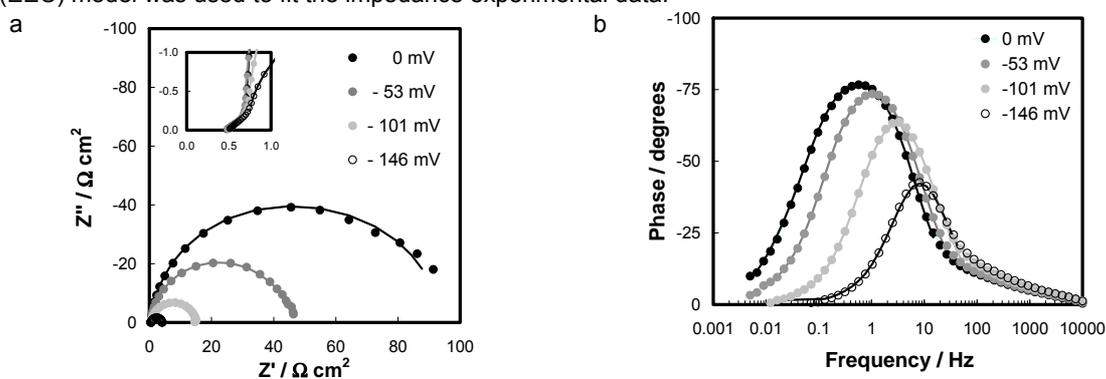


Figure 5. Impedance data obtained in 30 wt.% KOH solution at  $30^\circ\text{C}$  for Ni catalyst: a. Nyquist representation, a Bode representation of the phase angle as a function frequency

The real surface area of the fabricated cathodes can be estimated through the EIS results by means of the surface roughness factor ( $R_f$ ), which was calculated for each electrode by dividing  $C_{dl}$  by the double-layer capacitance of a smooth electrode,  $20 \mu\text{F cm}^{-2}$ . Thus, if it is subtracted the surface area effect, it is possible to differentiate the HER intrinsic catalytic activity of the material. For this purpose, Table 3 lists the exchange current densities normalized to the true surface area by dividing the value by the corresponding surface roughness factor. From Table 3 it can be confirmed that the Ni-Co and Ni-W have higher catalytic activity for HER than the Ni electrode as a consequence of the improvement in the intrinsic catalytic activity because the synergetic effect of alloying metals. However, in Ni-W the slight improvement showed in Tafel curves is due to the effect of surface area.

Table 4: Exchange current densities corrected with respect  $R_f$  for the investigated electrocatalytic coatings

Catalyst	Temperature			Catalyst	Temperature		
	30	50	80		30	50	80
Ni				NiMo			
$(j_0 R_f^{-1}) \cdot 10^3$	0.18	0.44	1.88	$(j_0 R_f^{-1}) \cdot 10^3$	4.96	17.93	53.99
NiCo				NiW			
$(j_0 R_f^{-1}) \cdot 10^3$	1.20	2.43	4.93	$(j_0 R_f^{-1}) \cdot 10^3$	0.14	0.33	0.98

#### 4. Conclusions

The electrocatalytic efficiency using pseudo-steady-state polarization curves and impedance spectroscopy techniques of the Ni, Ni-Co, Ni-Mo and Ni-W catalysts obtained by galvanostatic co-electrodeposition. The binary alloys show better catalytic activity than the Ni electrode with a similar roughness factor and a far better activity than a commercial smooth Ni electrode. From the  $E_a$  values obtained, it can be concluded that the Ni-Co electrode has the highest improvement in the intrinsic catalytic activity. The kinetic parameters obtained indicate that HER takes place by the Volmer-Heyrovsky mechanism. Values for exchange current densities for the investigated electrodes were in the range of  $10^3$  orders of magnitude higher than those values for the smooth Ni electrode. Results suggest to significant catalytic performance not only from the increase of the real surface area of electrodes, but also from the intrinsic catalytic effect.

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