# Nickel-Cobalt Alloys Electrodeposited at Controlled pH for Hydrogen Production in Alkaline Media (O-5H)

M. J. Gómez[1*], G.I. Lacconi[1], E.A. Franceschini [1**]

[1] *INFIQC-CONICET, Dto. de Fisicoquímica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria, 5000 Córdoba, Argentina.*

(*) Pres. author: melisa.julieta.gomez@gmail.com          (**) Corresp. author: estebanfranceschini@yahoo.com.ar

## 1. Introduction

Hydrogen has become an energy vector of interest, because it allows the storage of energy from different sources, particularly interesting when is coupled with renewable ones. The combustion of hydrogen generates only water, thus avoiding the emission of polluting gases that promote global warming. Hydrogen can be produced through the electrolysis of water, usually carried out in alkaline liquid electrolyzers (AEL), using nickel electrodes as catalysts for the hydrogen evolution reaction (HER). It is known that the formation of alloys with other transition metals, such as cobalt, generates a significant increase in the activity of the HER catalysts. The formation of alloys alters the position of the nickel "d" bands, and with them, its Fermi level. These new alloyed materials can be obtained as an electrochemical deposition coating by simply adding the precursor salts to the traditional Watts bath.

NiCo alloys possess distinctive mechanical, thermophysical and magnetic properties; and compared to pure nickel, NiCo deposits have higher hardness and better wear and corrosion resistance. Several publications evaluated their catalytic activity for HER in alkaline media, working with alloy coatings with different Ni/Co ratios [1]–[3]. All of them conclude that the HER at NiCo electrodes is superior to that of Ni. However, the correlation between the catalytic activities of the alloys and the structural properties is not exhaustively carried out. In a previus work [4], we study the NiCo alloy in electrochemical baths with different $Co^{2+}$ proportion and pH. Now we present a morfollogical and electrochemical study, using a modified nickel Watts bath, with a controlled pH.

## 2. Experimental

### 2.1 Materials

Hydrochloric acid (Cicarelli, PA grade), potassium hydroxide (Anedra, PA grade), nitric acid (Cicarelli, PA grade), sulfuric acid (Cicarelli, PA grade), ethanol (Cicarelli, 96%), acetone (Cicarelli, PA grade), cobalt (II) sulfate heptahydrate (Anedra, PA grade), nickel (II) sulfate hexahydrate (Anedra, PA grade), nickel (II) chloride hexahydrate (Anedra, PA grade) and boric acid (Merck, PA grade) were used as purchased, without prior purification. Milli-Q water was used for rinsing and solution preparation. AISI 316L stainless steel plates were used as substrate, partially covered with insulating tape to expose a surface area of 4 cm$^2$. The composition of the steel is: Cr 17%, Ni 12%, C 0.01%, Mn 2%, Si 0.75%, P 0.045%, S 0.03%, Mo 2.50% and Fe% rest.

### 2.2 Solution and Sample Preparation

The AISI 316L steel plates were pretreated with the cleaning method detailed in Gómez et al [4]. They were then coated with an adhesion layer, or nickel strike deposit, using a 225 g/L $NiCl_2 \cdot 6H_2O$ solution acidified to pH 0.5 with HCl, to improve the adhesion of the alloy layer. A second layer of nickel was electrodeposited on top of the strike layer but with the formulation of a modified Watts bath to obtain the coating of a NiCo alloy. For this bath, 280 g of $NiSO_4 \cdot 6H_2O$, 35 g of $NiCl_2 \cdot 6H_2O$, 45 g of $H_3BO_3$ and three different ratios of $CoSO_4 \cdot 6H_2O$ per liter, were used to synthesize the NiCo alloy. The proportions of $CoSO_4 \cdot 7H_2O$ were: 1.5, 3.5 and 15 mol % of the total moles of $Ni^{2+}$ present per liter. The samples are named in function of the bath composition. The pH of each solution was kept at 3.5 independet of the $CoSO_4 \cdot 7H_2O$ concentration. Nickel electrodeposition in every step was performed in a two-electrode cell with a nickel anode, by application of a - 0.05 A/cm$^2$ pulse at 55 °C, during 1800 s for the strike layer and 2700 s for the catalytic layer. The total coating thickness is about 75 μm, which includes 30 μm from the adhesion layer and 45 μm of the catalytic layer.

## 3. Discussion

### 3.1 Chemical and Structural Characterization

The morphology of the deposits obtained was established by SEM micrographs of the different NiCo alloy electrodes, which are shown in Figure 1. The images show the nominal compositions of $Ni^{2+}$ and $Co^{2+}$ in the baths (EDP). The metallic Ni and Co compositions can also be observed (EDS) and were determined with EDS. It is notable that Co deposition is preferential to Ni since the Co/Ni ratios in the deposits are significantly higher than the Co/Ni ratio used in the baths. This has been published as due to the formation of a CoOH film at the liquid-electrode interface, which hinders the adsorption of $Ni^{2+}$ on the cathode for its reduction [2], [3]. As the amount of deposited Co increases, it can be observed that the surfaces change from having a low relief with stepped structures and larger grains, to a higher relief with well-defined pyramidal shapes, with apparently smaller grains.

The crystalline structure of the coatings was determined by means of the diffractograms obtained by X-ray diffraction

for the different NiCo alloys, which can be seen in Figure 2. The peaks present at 2θ values of approximately 45.5° and 53° correspond to the (111) and (200) planes of nickel for a face-centered (fcc) cubic crystallization system. The intensities have been normalized with respect to the (111) plane of Ni. The absence of extra peaks is a first indication that the synthesized materials are true alloys. As the amount of Co increases, the decrease of the intensity of the peaks corresponding to the (200) planes is observed until disappearing for NiCo 15% mol. This implies a possible change of cristallographic sistem from fcc to hcp or a mixture between fcc and hcp.
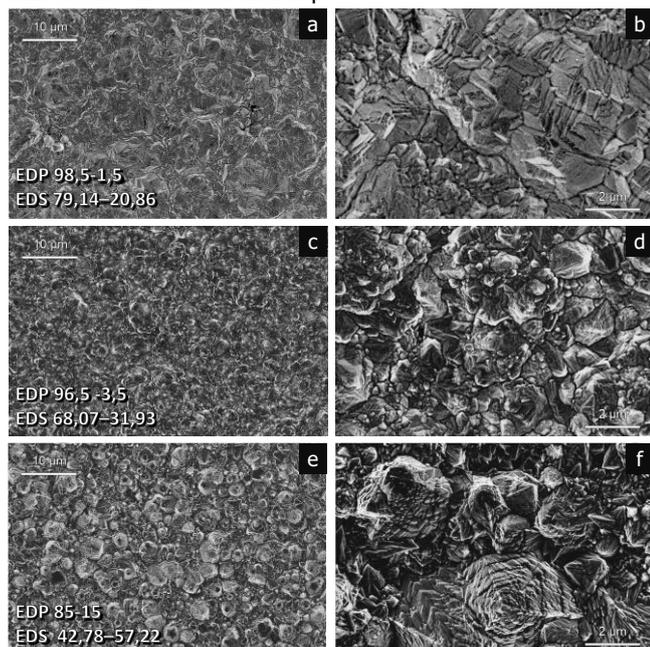


**Figure 1: SEM images of the surface of NiCo deposited plates, taken at 5 kV and at two different magnifications. The composition is indicated in each image as % mol Ni and Co: EDP corresponds to the nominal composition of the bath, EDS corresponds to the composition of the electrodeposits obtained by EDS.**
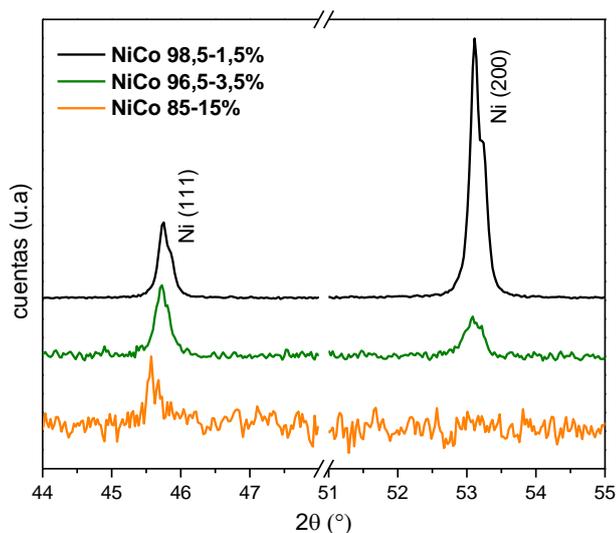


**Figure 2: X-ray diffractograms of the NiCo plates, obtained at 2θ values between 10° to 70° and amplified in the Ni signal zones.**

The roughness obtained by surface root mean square (RMS) of the samples was analyzed by confocal microscopy images at two magnifications: 1070x and 2132x, each one

contemplating a geometric surface of $(258\ \mu m)^2$ and $(130\ \mu m)^2$, respectively. Table 1 shows the measurements obtained for each NiCo sample and compares them with a pure Ni sample, electrodeposited with a Watts bath (Ni-Watts). The RMS values for the electrodes with deposited Co content of less than approximately 32%, do not differ significantly from those obtained for the Ni-Watts samples. For NiCo 1.5% mol the RMS is 1.4% higher and for NiCo 3.5%, 13.3% higher than for Ni-Watts. However, for NiCo 15% mol with 57.22% Co content in the alloy, the RMS increases significantly, being 55.7% higher than that of Ni. Such an increase is consistent with what was observed in SEM micrographs where the surface shows pyramidal structures with large unevenness.

Figure 3 shows the spectra obtained with Raman confocal spectroscopy for the as-deposited, fresh and aged NiCo alloys. The samples were subjected to an aging process for hydrogen production at -1.5 $V_{SCE}$ for 4 h at 25 °C in 1 M KOH. The fresh electrodes show no differences between each other, even though they possess different Co content, but a change is observed when the Raman spectra of the aged materials are analyzed. In all newly synthesized samples, the spectra contain signals between 400 and 1100 cm$^{-1}$ corresponding to NiO surface oxide and other non-stoichiometric nickel oxides. The CoO signals are presented as two broad bands that can be observed centered at 440 and 702 cm$^{-1}$.

**Table 1: RMS obtained at different magnifications: the average values of the Ni-Watts electrodes (0% Co) and of the different alloys synthesized are presented.**

| %Co$^{+2}$ (mol bath) | %Co$^{+2}$ (mol EDS) | RMS 1070x (μm) | RMS 2132x (μm) |
|---|---|---|---|
| 0 | 0 | 0.35 | 0.32 |
| 1.5 | 20.86 | 0.35 | 0.30 |
| 3.5 | 31.93 | 0.39 | 0.38 |
| 15 | 57.22 | 0.54 | 0.52 |

In all aged electrodes, hydroxide signals can be found in different regions of the spectrum. Both, Co(OH)$_2$ and Ni(OH)$_2$, have a signal at high wavenumbers, approximately at 3500-3650 cm$^{-1}$ corresponding to the stretching of the O-H groups. The presence of hydroxides is associated with the formation of passivation layers for HER.
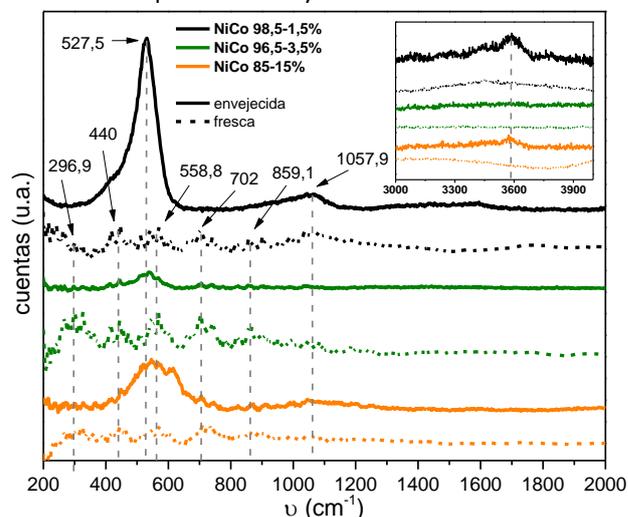


**Figure 3: X Raman spectra obtained for samples deposited with different Co ratios for NiCo alloys. Inset graph: magnification in the area where the O-H stretching signals are present.**

### 3.1.1 Electrochemical characterization

Electrochemical experiments were performed in a three-electrode electrochemical cell with a thermostatic jacket, using a large-area platinum foil as a counter electrode and a saturated calomel electrode (SCE) as a reference electrode (0.243 $V_{RHE}$). The electrolyte consisted of a deoxygenated 1 M KOH aqueous solution.

Cyclic voltammetries were performed to compare the effects produced on the current density before and after the aging process. The values of the current densities obtained at -1.5 $V_{SCE}$ are given in Table 2. Comparing these data, it is observed that the NiCo 3.5% mol electrode is the most active for HER at the two temperatures studied. At 25 °C, this electrocatalyst shows a current density 93.3% higher than NiCo 1.5% mol and Ni-Watts; and 41.4% higher than NiCo 15% mol. The current density values measured in the voltagrams of the aged plates are lower than for the newly synthesized ones, except for NiCo 15% mol where no variation is observed. This implies that, when using NiCo electrodes for hydrogen production, a deactivation is generated. This may be due to the formation of passivating layers of hydroxides of Ni and Co. On the other hand, as with Ni-Watts electrodes, it can be observed that the increase in temperature causes an increase in current density, and hence, the increase in the amount of hydrogen generated.

**Table 2: Current densities (j) obtained at -1.5 $V_{SCE}$ and onset potentials ($E_{OP}$), taken from cyclic voltammetries recorded at 5 mV/s, at 25 and 50 °C.**

| Temperature | 25 °C | | 50 °C | |
|---|---|---|---|---|
| Electrode | fresh | aged | fresh | aged |
| | j (A·cm$^{-2}$) a -1,5 $V_{SCE}$ | | | |
| Ni-Watts | -3.0.10$^{-2}$ | -2.6.10$^{-2}$ | -4.9.10$^{-2}$ | -5.5.10$^{-2}$ |
| NiCo 1.5% | -3.1.10$^{-2}$ | -2.6.10$^{-2}$ | -4.5.10$^{-2}$ | -4.1.10$^{-2}$ |
| NiCo 3.5% | -5.8.10$^{-2}$ | -5.0.10$^{-2}$ | -8.7.10$^{-2}$ | -8.1.10$^{-2}$ |
| NiCo 15% | -4.1.10$^{-2}$ | -4.2.10$^{-2}$ | -5.4.10$^{-2}$ | -5.5.10$^{-2}$ |
| Electrode | $E_{OP}$ ($V_{SCE}$) | | | |
| Ni-Watts | -1.03 | -1.03 | -1.02 | -1.03 |
| NiCo 1.5% | -0.84 | -0.82 | -0.85 | -0.74 |
| NiCo 3.5% | -0.96 | -0.75 | -0.96 | -0.75 |
| NiCo 15% | -1.08 | -0.82 | -0.96 | -0.78 |

The onset potentials ($E_{OP}$) of NiCo plates are lower than those obtained for Ni. If the aged NiCo plates are compared with the freshly synthesized ones, it can be observed that the $E_{OP}$ become less negative. The decrease in overpotential for $E_{OP}$ is an indication that less energy is required to start hydrogen production. Therefore, there will be a grater chance that, whith the same overpotential, a higher current density corresponding to HER will be achieved.

Figure 4 shows the chronoamperometric profiles obtained for NiCo alloys and compares them with Ni-Watts, in order to simulate electrode aging. The measured current density values indicate that NiCo alloys are 10 times more active than Ni-Watts, the most active being NiCo 3.5% mol.

## 4. Conclusions

NiCo alloy electrodes were synthesized using Ni-Watts baths modified with different proportions of CoSO$_4$·7H$_2$O:

1.5, 3.5 and 15% in mol of Co$^{2+}$. The synthesis was carried out on AISI 316L steel plates previously coated with Ni strike.

The evaluation by electrochemical experiments indicates that NiCo electrodes are notably more active for HER than Ni-Watts in alkaline medium. Particularly NiCo 3.5% is the one with the highest current density. In CVs, this electrode generates 93.3% more current at -1.5 $V_{SCE}$ than Ni-Watts, and in chronoamperometry it is 889% higher.

NiCo 3.5% is observed to have the highest (111)/(200) ratio while maintaining the fcc structure. These planes are associated with the presence of more active sites for hydrogen detachment in Ni cathode.

The presence of nickel and cobalt oxides, formed by exposure to air, was observed in all fresh electrodes. Once aged, the plates developed surface nickel and cobalt hydroxides which are associated with the formation of passivation layers.
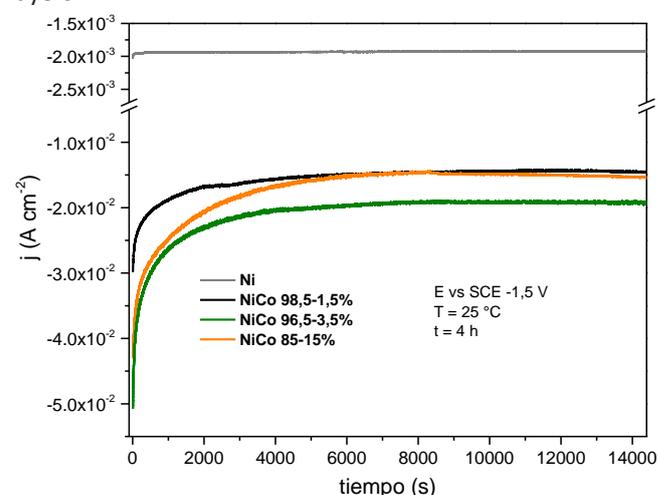


**Figure 4: Chronoamperometries performed on NiCo alloys and Ni-Watts in 1 M KOH at -1.5 V vs. SCE, at 25 °C for 4 hours.**

### References

[1] C. Lupi, A. Dell'Era, y M. Pasquali, «Nickel–cobalt electrodeposited alloys for hydrogen evolution in alkaline media», *Int. J. Hydrog. Energy*, vol. 34, n.º 5, pp. 2101-2106, mar. 2009, doi: 10.1016/j.ijhydene.2009.01.015.

[2] C. Lupi, A. Dell'Era, M. Pasquali, y P. Imperatori, «Composition, morphology, structural aspects and electrochemical properties of Ni–Co alloy coatings», *Surf. Coat. Technol.*, vol. 205, n.º 23-24, pp. 5394-5399, sep. 2011, doi: 10.1016/j.surfcoat.2011.06.002.

[3] A. Bai y C.-C. Hu, «Effects of electroplating variables on the composition and morphology of nickelÁ/cobalt deposits plated through means of cyclic voltammetry», *Electrochimica Acta*, p. 10, 2002.

[4] M. J. Gomez, E. A. Franceschini, y G. I. Lacconi, «Ni and Ni x Co y Alloys Electrodeposited on Stainless Steel AISI 316L for Hydrogen Evolution Reaction», *Electrocatalysis*, vol. 9, n.º 4, pp. 459-470, jul. 2018, doi: 10.1007/s12678-018-0463-5.