



## Evaluation of production electrocatalyst for hydrogen electrolysis from water

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**Abstract:** This paper analysed three specific ternary alloys, electrodeposited on the cathode and the anode of alkaline water electrolysis, called electrocatalysts. The analysis was done by monitoring the hydrogen production (mL/min) from the electrolysis of water at different current densities (mA/cm<sup>2</sup>). Three different electrocatalysts were analysed, at the cathode (Ni, Pt and Mo) and the anode (Ni, Co and Cr). The difference between the cathode electrocatalyst was given by the composition of the nickel (54.4 wt% and 74.4 wt%), which represented a change in the structure of the phases in the electrode surface. No significant difference was found between the two different electrocatalysts at the cathode, despite the higher content of nickel and greater influence on hydrogen production. A 30% increase in the production of hydrogen with respect to the control was reached, the presence of the electrocatalyst at the anode and presence of nickel in the cathode electrocatalyst.

**Keywords:** electrocatalysts, hydrogen, electrolysis, electroplating.

### Introduction

Nearly two thirds of the energy used today is from fossil fuels. These fuels have created the problem of air pollution and global climate change, so solutions involving alternative fuels have been proposed. Hydrogen is the most beneficial in terms of reduced emissions and high efficiency. Hydrogen can be produced in various ways, through natural gas, coal, water electrolysis, biomass, solar, wind or nuclear<sup>1</sup>. Of the different production methods, water electrolysis is the only industrial technology that produces hydrogen with zero emissions and available at the moment<sup>2</sup>. In the future, the electrolysis of water will become the only source of energy that produces a sufficient amount of hydrogen to supply energy for all the vehicles in the

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US, which was expected to hit 250 million in 2010<sup>3</sup>. Since the electrolysis of water is economic and efficient, reducing the potential of the electrolytic cell is vital<sup>4</sup>. The voltage required in the cell depends mainly on hydrogen and oxygen overvoltage, and the electrolytic resistance of the electrolyte used. The surge can be reduced with the use of an appropriate electrocatalyst, while the resistance of the electrolyte can be reduced by using more conductive substances (e.g. PEM's) or by increasing the temperature of the solution<sup>5</sup>. Many transition metal alloys with binary and ternary compositions have been studied as electrodes in water electrolysis. The electrocatalytic activity of the alloys depends mainly on the surface area<sup>6</sup>. A careful review of the literature shows that innovations are restricted to a small number of systems. Among them, nickel alloys, either in crystalline or amorphous forms, have shown to be successful as cathode materials, while the Ni-Co alloys show very good electrocatalytic activity as anode catalysts<sup>7,8</sup>. On the other hand, deposition at high current density is used to obtain a high surface area<sup>9</sup>. This paper discusses three electrocatalysts, two for the cathode and one for anode in alkaline water electrolysis. The parameter is the difference in amount of hydrogen produced in mL/min. The metals that serve as electrocatalysts were selected for their availability, their ability to be electrodeposited on the electrodes and their high electrocatalytic activities as referenced in the literature<sup>9-16</sup>. The contribution of this work is the use of ternary alloys, i.e. three components to be used as electrocatalysts.

## Results and discussion

### Electrodeposition conditions and weight of the electrocatalyst

Table 1 presents the optimum conditions found by assay and error for the electrodeposition of metals on the stainless steel electrodes according the electrocatalyst deposited.

**Table 1.** Optimal conditions of electrodeposition, according to the electrocatalyst.

Name of Electrocatalyst type	Current density [mA/cm <sup>2</sup> ]	Temperature [°C]	Time [hours]
Type A cathodic	200	60	1
Type B cathodic	100	20	1
Anodic electrocatalyst	250	60	2

The quantity of electrocatalyst deposited varied with the metals used. Table 2 shows the amount of electrocatalyst deposited, determined by the electrode weight difference before and after electrodeposition.

**Table 2.** Quantity of electrocatalyst deposited.

Electrocatalyst type	Quantity of Electrocatalyst deposited[g]
Type A cathodic	0.04±0.030
Type B cathodic	0.05±0.010
Anodic electrocatalyst	0.03±0.001

**Results of the hydrogen production of the electrocatalyst**

Using stainless steel electrodes, with pretreatment, but without electrocatalysts was obtained a hydrogen production  $8.725 \pm 0.0025$  mL/min to  $160 \text{ mA/cm}^2$  and a density of  $200 \text{ mA/cm}^2$ , and with electrocatalyst, hydrogen production was  $10.800 \pm 0.0000$  mL/min. These two facts were established as the benchmark experiments for electrodes with electrocatalysts. Following are the results of the production of hydrogen and the percentage difference compared to the baseline data, when type A and B electrocatalyst was used at the cathode in the presence or absence of the anode electrocatalyst. These results were obtained with two different current densities, 160 and  $200 \text{ mA/cm}^2$ . The results are summarised in Table 3.

**Table 3.** Experimental scheme for the determination of hydrogen production using several electrocatalyst in the electrodes.

Current density [mA/cm <sup>2</sup> ]	Type of cathodic catalyst	Presence of the anodic catalyst	Hydrogen production [mL/min]	Percentage difference with the reference [%]
160	None	None	8.725±0.0025	0.0
200	None	None	10.800±0.0000	0.0
160	A	No	10.875±0.0025	24.6
200	A	No	13.825±0.0025	28.0
160	B	No	10.625±0.0025	21.8
200	B	No	13.500±0.0000	25.0
160	A	Yes	11.225±0.0025	28.7
200	A	Yes	14.050±0.0033	30.1
160	B	Yes	10.900±0.0000	24.9
200	B	Yes	13.950±0.0033	29.2

From these results several important factors can be determined:

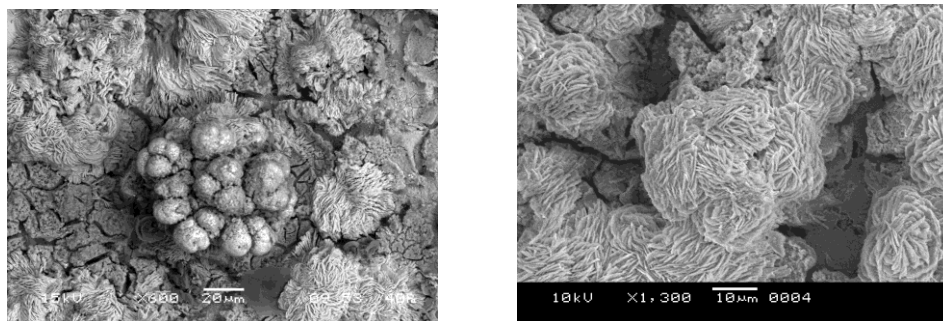
- (i) When the current density is higher, the production of hydrogen using the electrocatalysts increases. 3.1% more hydrogen was obtained, on average, at  $200 \text{ mA/cm}^2$  than  $160 \text{ mA/cm}^2$ .

- (ii) The electrocatalyst at the anode has a definite influence on the water electrolysis reaction. 3.4% more hydrogen was obtained, on average, by using an anodic electrocatalyst than not using it,
- (iii) In the same way, the type A cathode electrocatalyst is more effective than type B in the production of hydrogen, however the difference is not significant. Thus, we obtained 2.6% more hydrogen, on average, using the type A cathode electrocatalyst than with type B,
- (iv) When using the cathodic electrocatalyst type A, and anodic electrocatalyst with a current of  $200 \text{ mA/cm}^2$  it was determined that hydrogen production was 30% higher. This is the optimum condition for hydrogen production found in this study.
- (v) For a longer current density, there will be a greater production of hydrogen, using the electrocatalyst synthesized in this work just as shown in the images of the figure 1.
- (vi) Hydrogen production was always higher with type electrocatalyst at the cathode and the anode electrocatalyst than with the other options. However, it is emphasized that the production of hydrogen with type B cathode and with the anode electrocatalyst has a tendency to surpass the first option at higher current densities. Even at  $200 \text{ mA/cm}^2$  these two options only have a difference of 0.9% in hydrogen production.
- (vii) Similarly, the choice of type B and non-electrocatalyst at the anode always results in lower hydrogen production than the other options.
- (viii) The results of table 3 suggests that at higher current densities all the options analysed in this study tended towards similar amounts of hydrogen production.

Our results show that are comparable to those reported with other researches of literature<sup>17</sup> but in this work we obtained hydrogen production levels with sample experiment and facility to be scaled to pilot plant level, which gives our research additional value.

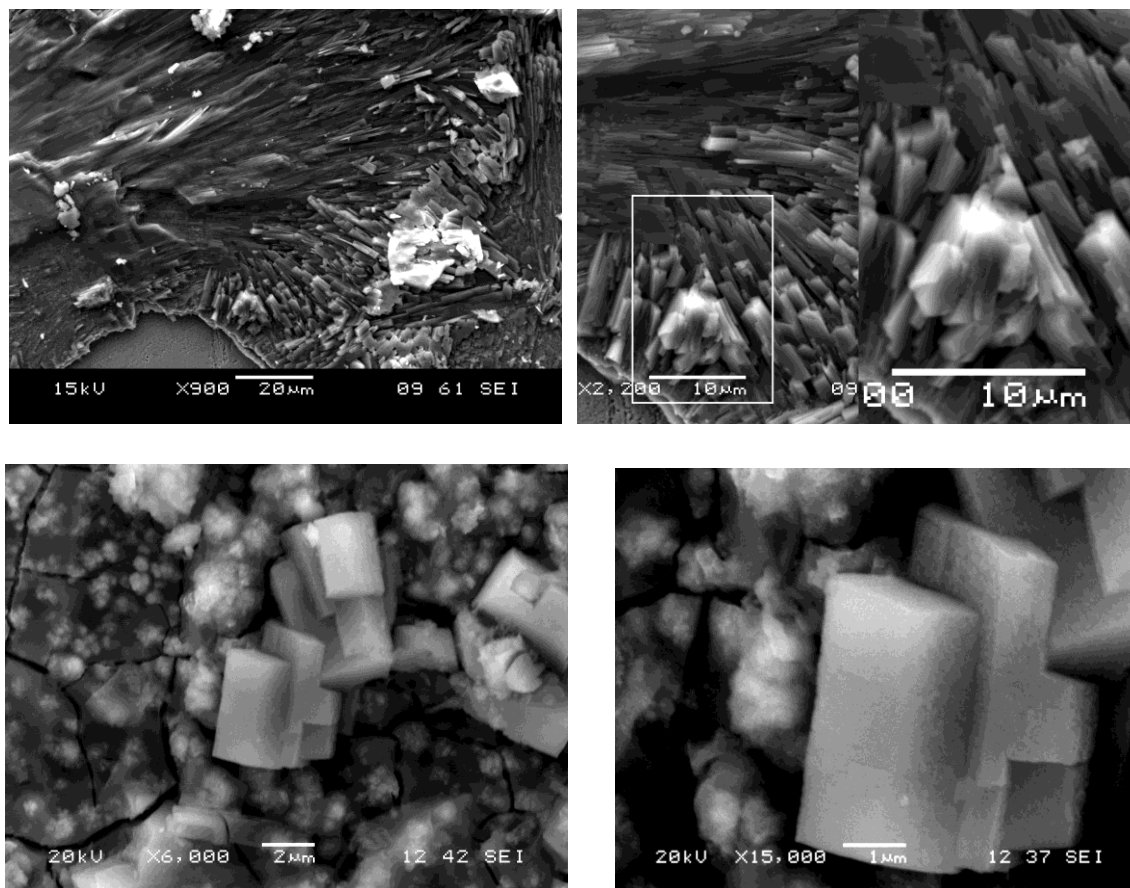
### Surface morphology of the electrocatalysts

For the production of hydrogen were relevant the types A of electrocatalysts used at the cathode and the anode. The surface morphology was determined by scanning electron microscopy (SEM). In Figure 1, two SEM images of the surface of the type A electrode are provided. The first image is taken at a magnification of 600X and the second at 1200X.



**Figure 1.** SEM images of the electrocatalyst superface type A used at the cathode

In Figure 2, four images of the surface of the anode electrocatalyst used are shown. In order from left to right and top to bottom, the first image is taken at 900X, the second at 2200X, the third at 6000X and the fourth at 15000X.



**Figure 2.** SEM images of the surface of the anode electrocatalyst used

## Conclusion

The most important conclusion was that there was an increase in hydrogen production by electrolysis of water by the electrodeposition of metals at the electrodes. This meant that it was possible to reduce the over-voltage production of hydrogen and oxygen by electrocatalytic action of electrodeposited alloys. Thus hydrogen production increased with respect to the reference values, by between 22 to 30%. The cathode electrocatalyst type A, provided the best results, but the difference to electrocatalyst type B was only close to 0.9% in the production of hydrogen. The anode electrocatalyst showed a 3.4% improvement in the overall response, regardless of the cathode electrocatalyst used, because the kinetics of hydrogen evolution reaction is influenced by the oxygen evolution reaction, i.e. if you reduce the over-voltage of oxygen production also makes the hydrogen and vice versa. The cleaning of the surface where electrodeposition is to take place is a fundamental element because it completely changes the characteristics of the shell, with regards to adherence and increased surface area, since no growth centres are created by the same

lack of grip. We implemented the results of other investigations for the design of the electrolytic cell, the electrode and that met the needs required. Many studies have been conducted on electrocatalysts for water electrolysis, but the contribution of this project is to study a combination of metals that so far have not been used as electrocatalysts. The study of electrocatalysts in the production of hydrogen requires further analysis, because there are many variables in this case study that were not analysed and could be the subject of further investigation, such as the distance between the electrodes, the electrolyte used in the electrolyte solution, electrode material, plating conditions, the influence of temperature, pressure, and, of course, the creation of new electrocatalysts with other metal alloys.

## Experimental

### Characterisation and preparation method

For the electrolysis of water, 304 stainless steel electrodes with a thickness of 1.2 mm (size 18) are used, with dimensions of 2.5 cm x 10 cm x 0.12 cm, with an average area of  $5.9 \pm 0.1 \text{ cm}^2$  and an average weight of  $2.2 \pm 0.1 \text{ g}$ . These electrodes served as a support for the electrocatalyst in the water electrolysis reaction. Stainless steel electrodes were subjected to pre-cleaning to ensure good adhesion of the electrocatalyst. This cleaning process consists of four steps:

- (i) polishing: where the electrodes were polished with fine sandpaper removing the impurities in the metal and improving the adherence of the electrocatalysts
- (ii) electrolytic cleaning: where electrolysis was carried out with stainless steel electrodes as the cathode. A common soap solution and potassium hydroxide (KOH) were used at a current density of 50 milliamps per square centimetre ( $\text{mA}/\text{cm}^2$ ) for 3 minutes. This clears the electrode of any residual fat that might impede the electroplating,
- (iii) neutralization / activation: the electrodes were placed in a solution of hydrochloric acid (HCl) to 30% by volume, for 1 minute. This neutralises the solution left by the previous procedure, and also activates the electrode surface to improve adhesion in the next step
- (iv) activation with nickel (Ni): where a thin layer of Ni was electrodeposited on the electrodes. The stainless steel electrode was placed as the cathode and a Ni metal plate as the anode in a solution of nickel chloride hexahydrate ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ) and sulfuric acid ( $\text{H}_2\text{SO}_4$ ), for 2 minutes at  $50 \text{ mA}/\text{cm}^2$ . The last step improves the adhesion of the electrocatalyst in the Ni layer, because this is superior to stainless steel.
- (v) Similarly we get the Mo and Ni electrocatalysts, the respective salts are used, using the same current density level.

### Electroplating

Electric potential is applied to the stainless steel electrodes when they are immersed in salt solutions of metals. This allowed electroplating a thin layer of the electrocatalysts to the electrodes. The concentrations of the metal salts in the solutions are directly related to the composition of the electrodeposited metal. These metals act as electrocatalysts during the electrolysis of water. We used graphite as the anode as an inert material and stainless steel electrodes were used as the cathode because there were deposited metal salts. The solution of

metal salts was acidified with  $\text{H}_2\text{SO}_4$  because the production of hydroxide ions facilitates the precipitation of metal ions. The salt solutions of metals contain hydrazine sulfate ( $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ ) to 0.1 molar (M), which is a strong reducing agent that easily donates electrons and facilitates electrodeposition<sup>15</sup>. Adding this type of compounds is important in reduction processes occur because it requires that an adequate supply of electrons in electrocoat these species should be added to improve the reduction.

The electroplating is conducted under certain parameters of current density, temperature, agitation of the solution and the electrodeposition time, etc. These parameters were determined in relation to the largest surface area and adhesion to the electrode. These properties were measured by observation and physical contact of the electrodeposition on stainless steel electrodes, and its adhesion was tested by using a test electrolysis in KOH solution (30% by weight). Optimal conditions varied depending on the electroplating solution used and was determined by trial and error. Finally, with continuous agitation of the solution of metal salts during the electrodeposition increased the weight of the electrocatalyst deposited on the stainless steel electrodes.

### Composition of electrocatalysts

Two cathodes were used as water electrolysis electrocatalysts (Type A and Type B), consisting of the same metals, platinum (Pt), nickel (Ni) and molybdenum (Mo), but with different compositions of Ni and Mo, as shown in Table 4.

**Table 4.** Salts of metals used in the solutions for the cathodic electrocatalyst, its concentration and metals concentration.

Type	Electrodeposited Metal Salts	Solution Concentration molar	Metal Concentration [% weight]
A	$\text{PtCl}_4$	0.0005	1.2
	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	0.1	74.4
	$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$	0.02	24.3
B	$\text{PtCl}_4$	0.0005	1.2
	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	0.1	54.4
	$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$	0.5	44.5

We used two different compositions for the electrocatalysts in the cathode in order to determine the influence of a higher content of Ni in the hydrogen evolution reaction (HER). The Mo has to be electroplated simultaneously with an iron group metal (Fe), but lost grip in the deposition. In addition, its content in the electrocatalyst cannot exceed 45% by weight, because above this low efficiencies are experienced and the HER cathode is affected<sup>11-16</sup>. For the anode one electrocatalyst was used, composed of nickel (Ni), cobalt (Co) and chromium (Cr), as shown in Table 5.

Unlike the cathode electrocatalysts, Co, Cr and Ni, present a good performance in the kinetics of the oxygen evolution reaction (OER).

**Table 5.** Salts of metals used in the solutions for the anodic electrocatalyst, its concentration and metals concentration.

Electrodeposited Metal Salts	Solution Concentration molar	Metal Concentration [% weight]
NiCl <sub>2</sub> ·6H <sub>2</sub> O	0.1	34.6
CoCl <sub>2</sub> ·6H <sub>2</sub> O	0.1	34.7
CrCl <sub>3</sub> ·6H <sub>2</sub> O	0.1	30.7

**Hydrogen production**

The result of this study was to evaluate the production of hydrogen (H<sub>2</sub>) measured in millilitres per minute (mL/min), obtained from the alkaline water electrolysis (KOH solution 30% by weight) in a built and design electrolytic cell in our laboratory. The electrolytic cell allows the easy exchange of different electrodes for testing and has a burette (resolution 0.1 mL) to measure the hydrogen produced at the cathode during electrolysis. It has a porous membrane that allows free circulation of the electrolyte and separates the two electrodes, cathode and anode. Figure 3 shows a scheme of the setup and the schematic of the electrolytic cell.

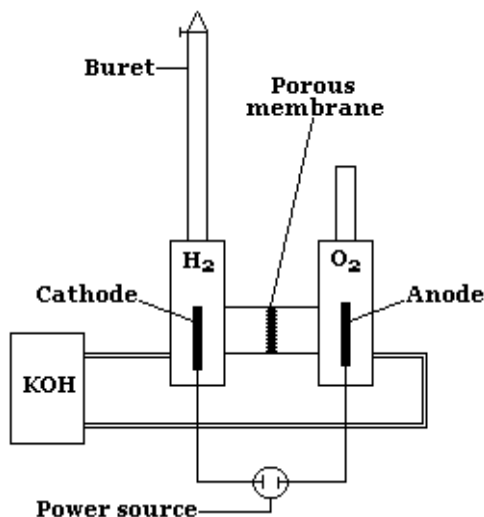
**Figure 3.** Explanatory scheme of electrolytic cell.

Table 6 presents the experimental scheme which measured the production of hydrogen, using stainless steel electrodes with electrocatalysts, types A and B, at the cathode, in the presence or absence of an electrocatalyst at the anode and with a control without any electrocatalyst. Each of these experiments was carried out with two different current densities, 160 and 200 mA/cm<sup>2</sup>. The values of current density were established in previous experiments, were tested by several orders of magnitude and that will be chosen at the end showed layers on electrodes attached better.



**Table 6.** Experimental scheme for the determination of hydrogen production using several electrocatalysts in the electrodes.

Current density [mA/cm <sup>2</sup> ]	Type of cathodic catalyst	Presence of the anodic catalyst
160	None	None
200	None	None
160	A	No
200	A	No
160	B	No
200	B	No
160	A	Yes
200	A	Yes
160	B	Yes
200	B	Yes

There were four repetitions of each of these experiments and the average was used for the comparison chart of the results. In total 40 experiments were conducted.

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