



SYNTHESIS AND CHARACTERIZATION OF NI-MO ELECTRODES FOR THE HYDROGEN EVOLUTION REACTION

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ABSTRACT

Following the line of previous investigation that proved that Ni-Mo deposits show potential as electrocatalyst, Nickel-Molybdenum alloys were electrodeposited using current pulse of variable intensity and duration on vitreous carbon to measure their catalytic activity in the electrocatalysis of the hydrogen evolution reaction (HER) in water electrolysis. In this work the electrocatalytic activity of particles deposited using current pulses from 15 mA to 400 mA/cm² and pulse times of 1 to 5 seconds from a solution of NiSO₄ and Na₂MoO₄ was investigated. The deposited material was characterized for the HER using Cyclic Voltammetry in a 0.78 M solution of H₂SO₄. The material deposited with a current pulse of 71 mA/cm² has the highest activity for the production of hydrogen; with a value of exchange current during the HER of 1.82×10^{-3} A/cm² at -0.9Volts (vs. Hg/Hg₂SO₄) compared to an exchange current density of 2.31×10^{-5} A/cm² observed when using a glassy carbon electrode. Cyclic voltammograms revealed that two types of materials with different electrocatalytic activities, oxidation potentials and electrochemical stability were present in the deposit. Each possesses different electrocatalytic activity for the HER and completely different oxidation potentials and electrochemical stability. The material that shows the greatest catalytic activity has also the disadvantage of being highly unstable; the elimination of the most active material reduce the activity during HER almost 90%. The next step of the research will focus in the characterization of the deposits to identify the morphology, composition and size of the two different materials present in the deposit of Ni-Mo.

Key words: NiMo alloys, Hydrogen evolution reaction, electrocatalysis.



1. INTRODUCTION

One of the biggest challenges that we face today is the need to shift our energy consumption which currently is heavily dependent on fossil fuels to a more environmentally friendly and sustainable source of energy. The world energy demand is a natural consequence of our search for economic wealth and technological development but it is also tied to an unbalanced increase in the concentration of CO₂ in the atmosphere, responsible for the greenhouse effect, with the direct consequence of an steady increase in the average temperature of the Earth [1, 2]. Nevertheless, the cost of fossil fuels will only increase as these reserves significantly decline, bounding most of the current development of alternative energy sources to a cost-effective target. Among the proposed alternatives, hydrogen is a fuel with zero emissions of greenhouse gases (GHG), which has generated great interest in its use. To make its use feasible it is necessary to develop a method of obtaining it environmentally clean and economically viable. The use of solar energy in the electrolysis of water represents a process that is completely sustainable and environmentally friendly [3].

The hydrogen evolution reaction (HER) is essential in this process. The cost efficiency of the production of hydrogen using this method is limited by the efficiency of the energy conversion and the cost of the materials used in the hydrogen evolution reaction, in particular the electrocatalysts for which precious metals are commonly used [4]. As alternatives to platinum, some of the most important and studied metal catalysts are nickel and binary or ternary alloys are Ni-V, Ni-Ti and Ni-Mo [5, 6, 7]. Many studies report the particular catalytic activity of the Nickel Molybdenum (Ni-Mo) system for the HER. This system has demonstrated superior performance [7] and long term stability [8] compared bare nickel and other nickel alloys, requiring lower overpotentials [7]. In addition, Crespo et al. showed that nanoparticles of Ni-Mo deposited on a glassy carbon electrode presented a current exchange density of 3.09×10^{-4} A/cm² compared to 2.6×10^{-6} A/cm² for Nickel [9].

2. EXPERIMENTAL PART

The electrolytic bath used for deposition of Nickel-Molybdenum was as follows: 0.2M $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich), 0.06M $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (Mallinckroft Chemical Works), 0.136M $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ (Baker Analyzed Reagent) and deionized water; the pH was adjusted to 9.0 adding NH_4OH . This bath was prepared following the compositions used by Crespo. [9]

2.1 Electrodeposition on glassy carbon (GC) electrodes

All experiments were performed using a three-electrode arrangement connected to an EG&G PAR potentiostat/galvanostat, model 273A. The working electrode was made from a glassy carbon rod. The rod was encapsulated in a resin and only its cross section was exposed ($7 \times 10^{-2} \text{ cm}^2$) and polished with alumina powder with particle diameters of 1, 0.1 and $0.02 \mu\text{m}$. The electrode was polished for 30 seconds on each particle size. After each polishing process, the electrode was rinsed with deionized water and cleaned by immersion in an ultrasonic bath for 30 seconds. The reference electrode was a $\text{Hg}/\text{Hg}_2\text{SO}_4$ electrode (-0.641V vs. SHE) and the auxiliary electrode was constructed with a platinum mesh. All three electrodes were fitted into a Teflon cap to hold them in position and placed in a glass cell with 50 mL of the solution. Current pulses of varying intensity and duration were applied in order to deposit the nickel and molybdenum ions from the electrolytic bath. Each deposition experiment was performed in triplicate to verify reproducibility of the results. The current densities used for the electrodeposition experiments were in the range of 15 to $400 \text{ mA}/\text{cm}^2$.

2.2 Measurement of the electrocatalytic activity of the deposits

In order to assess the electrocatalytic activity of the Ni-Mo deposits previously obtained, each electrode was transferred to a 0.78M H_2SO_4 solution, and cyclic voltammetry experiments were carried out. A potential sweep from the open circuit potential of the system (usually -0.4V

vs Hg/Hg₂SO₄) to -0.9V and back to the starting potential was performed. The activity of the deposit was a direct measure of the current density observed at a fixed overpotential of 100 mV.

3. RESULTS AND DISCUSSION

3.1 Polarization potential curves

The polarization potential of the electrode was recorded during the constant current density pulse. It was observed that the potential curves were very reproducible and in most cases closely coincident. Figure 1 shows the polarization curves obtained after applying a current density of 50mA/cm² with a pulse length of two seconds. This curve shows that the electrode rapidly polarizes and then presents a recovery towards a steady state. These characteristics respectively correspond to the nucleation and growth processes of the deposit and the development of a concentration gradient at the surface of the electrode.

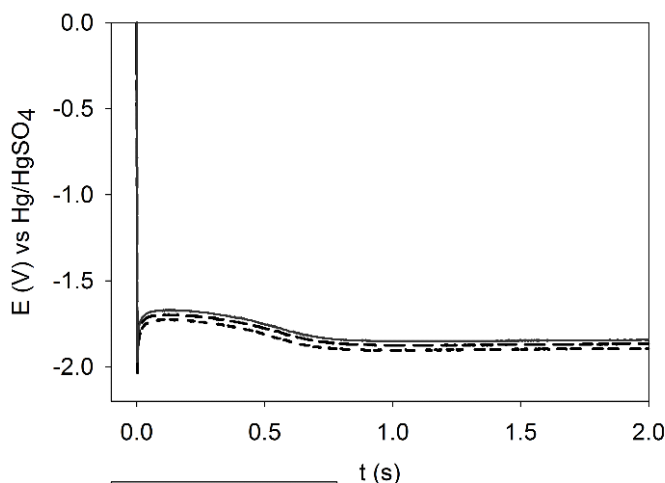


Figure 1. Polarization curves for a glassy carbon electrode at 50 mA/cm² with a pulse duration of two seconds. The curves obtained in three different experiments practically lay on top of each other, confirming the macroscopic reproducibility of these results.

The polarization potential curves at several current pulses are shown in Figure 2a. It can be observed that at current densities above 35 mA/cm² a fast polarization leading to a minimum and a recovery towards a steady state are obtained, but at this and higher current densities the potential drops again and a second minimum is observed at longer times. This is best shown in Figure 2b, where the time is plotted in logarithmic scale. This observation suggests that two different materials were deposited at current densities above 35 mA/cm².

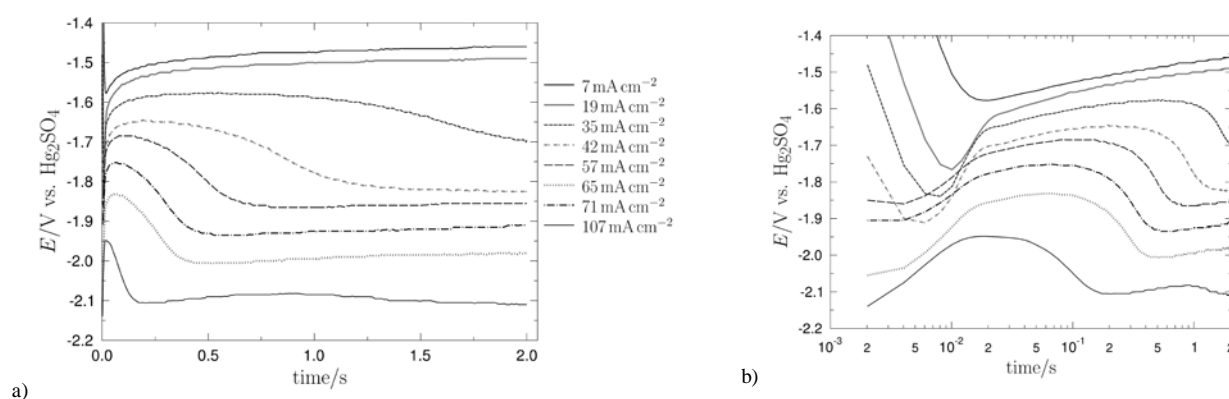


Figure 2. a) Polarization curves for a glassy carbon electrode resulting from fixed current pulses from 7 to 107 mA/cm² pulse. b) The time dimension in plot a) is shown in logarithmic scale to emphasize the presence of two potential minima observed in these experiments.

3.2 Electrochemical characterization of the deposits

The Ni-Mo electrodeposits were taken into a 0.78 M H₂SO₄ solution in which cyclic voltammetry experiments were carried out, from open circuit potential to -0.9 V and back towards 0.2 V. All potentials are referred to Hg/Hg₂SO₄ reference electrode. In the scan towards more positive potentials two irreversible oxidation processes were observed. The first (Ia) is observed at a potential of -241 mV and the second (IIa) at a potential of 128 mV. This observation indicates the presence of two different materials at current densities above 35 mA/cm² and is consistent with the polarization curves shown in Figure 2b. Figure 3 shows cyclic voltammograms of a deposit obtained with a two seconds pulse at a current density of 71 mA/cm². Three consecutive cycles were performed. The first cycle started at an open circuit potential of

−0.4V towards −0.9V and an exponential increase in current was observed corresponding to the evolution of hydrogen in the system. In a subsequent cycle, performed immediately after, was taken to −0.9V and then to a potential of 0.2V. An anodic peak was observed at a potential of −241 mV, corresponding to oxidation of the deposit called Ia. A second peak, smaller and wider is also observed. In the third cycle, a dramatic decrease in the current at −0.9V was observed, indicating that the activity of the material has dropped almost 80%. In the sweep towards positive potential only the IIa peak is observed this time, slightly shifted towards more negative potentials. These observations suggest that most of the material associated with the anodic process Ia had already been removed during the second cycle. Not only that, this observation indicates that from the two types of deposits obtained, this has the highest electrocatalytic activity (Ia) but is not stable at potentials higher than −0.2V.

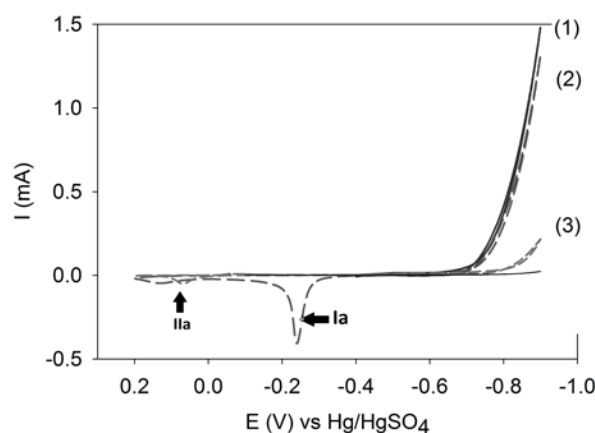


Figure 3. a) Cyclic voltammetry of Ni-Mo deposit obtained with a pulse of current density of 71 mA/cm² and a pulse length of 2s. Three consecutive cyclic voltammetry are shown. (1) First cycle is run from −0.4V to −0.9V to observe the hydrogen evolution current (2) In the second cycle the switch potential is 0.2V. Two anodic peaks denominated Ia and IIa are observed (3) In the third cycle the current corresponding to the hydrogen activity has substantially decreases, the process Ia is no longer observed and the IIa is maintained and has slightly shifted towards more negative potentials.

Considering these observations it can be deduced that two entirely different materials, which have different electrocatalytic activities for hydrogen evolution are present in the deposit. In the following, we will refer to these deposits as Ia, for the most active which oxidizes at −241mV and IIa for the material which is oxidized at 128mV vs. Hg/Hg₂SO₄.

Performing similar experiments as discussed above with deposits obtained at different current densities it was observed that the area under the peak corresponding to oxidation of Ia material is larger when higher current pulses are used, indicating that the amount of this deposit increases with the intensity of the current pulse. On the other hand, the area under the peak in process IIa remains essentially constant suggesting that once that surface of the electrode is completely covered with this deposit the material II will start depositing (See Figure 4).

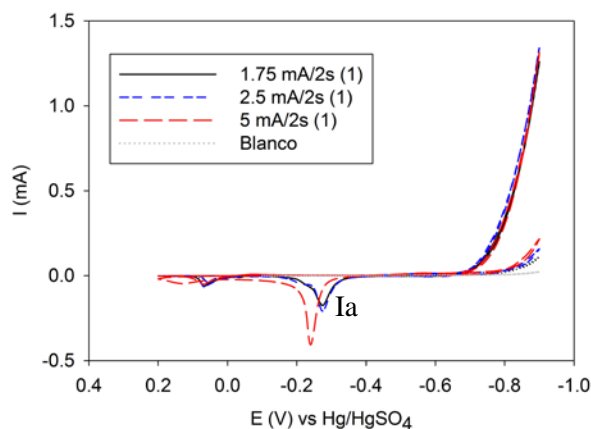


Figure 4. Cyclic voltammetry of deposits obtained with current pulses densities of 25, 35 and 71 mA/cm². Notice the differences in the areas for peak Ia.

3.3 Electrocatalytic activity of the deposits

Electrocatalytic activity for hydrogen evolution was determined of all the deposits obtained. Figure 5a shows the cyclic voltammetry of materials obtained at different current pulses. The current measured at a given potential is a relative measure of the speed at which hydrogen is reduced on the electrode surface modified with electrodeposition of Ni-Mo, and therefore of its electrocatalytic activity. Figure 5b shows a correlation between the current measured for the corresponding to the HER at a potential of $-0.9\text{V vs. Hg/Hg}_2\text{SO}_4$ and the density of current used in the preparation of electrodeposit. It can be observed that the activity of the deposits rapidly increases as the current density of the pulse used increases and reaches its largest activity for the

electrodeposits prepared with current densities between 70 to 100 mA/cm². The activity of the deposits obtained at currents greater than 100mA/cm² remains practically constant.

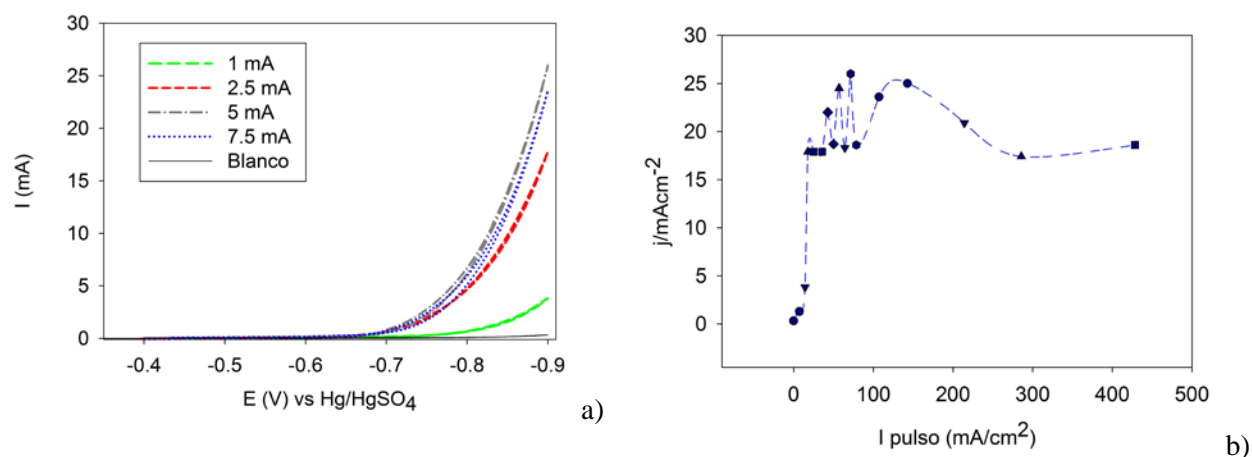


Figure 5. a) Cyclic voltammetry showing HER for deposits obtained with current pulses densities of 25, 35 and 71 mA/cm². b) The current density measured at -0.9V in the cyclic voltammetry experiments is plotted against the current density of the pulse used to obtain the deposit, showing that the highest activities are obtained at current densities between 70 and 100mA/cm².

4. CONCLUSIONS

It was found that nickel-molybdenum deposits obtained by pulsed current have an activity for hydrogen evolution. The material deposited with current density pulses between 70 and 100 mA/cm² and 2 seconds in length showed the highest activity, with a current density of 26mA/cm² at -0.9V vs. Hg/Hg₂SO₄. It was determined that during the deposition process two different materials were deposited, namely I and II, showing different oxidation potentials and stability. These materials also have different activities for the hydrogen evolution reaction, being material I at least four times more active than material II. A thorough characterization of the composition and morphology of the deposit is needed to fully determine the differences between these two different materials.

5. ACKNOWLEDGEMENTS

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