

**9th International Symposium on New Materials and Nano-Materials for  
Electrochemical Systems  
XII International Congress of the Mexican Hydrogen Society  
Merida, Mexico, 2012**

**Electrocatalytic Properties of NiMo Nanoparticles for the Hydrogen Evolution Reaction**

Savidra Lucatero, Gabriel Tamayo, Diego Crespo, Ernesto Mariño and Marcelo Vide\*<sup>\*</sup>

Tecnológico de Monterrey, Monterrey, N.L., Mexico cp 64849.

Corresponding author: (52) 81 83284489, mvidea@itesm.mx

**ABSTRACT**

Previous work recently presented by our group focused on the electrocatalytic activity of NiMo alloys for the hydrogen evolution reaction (HER). The performance of electrodeposits fabricated by means of current pulses from a binary Ni-Mo electrolyte was characterized by cyclic voltammetry. The deposition time was kept constant at 2 seconds in all cases, whereas the pulse current density was varied in the range of 7 to 107 mA/cm<sup>2</sup>. As a follow-up work, this investigation gathers information on compositional analysis and morphological features of electrodeposits. Electron microscopy imaging indicated that at the electrodeposition conditions utilized, the formation of nanoparticles (NPs) was favored; NP size ranged between 30 to 50 nm and was not significantly affected by variations in the intensity of the current pulse. Compositional analysis of the deposits suggested that Ni content in the electrodeposits was sensitive to changes in the applied current density, whereas Mo content was unaffected. The presence of oxygen within the materials suggested that oxide formation is highly probable. The electrosynthesis of two different catalytic materials was indicated by electrochemical characterization of the deposits; each showing different electrocatalytic activity, oxidation potential and electrochemical stability. The material with the greatest catalytic activity has also the disadvantage of being highly unstable, since its elimination reduces almost completely the activity for the HER. Ongoing work on compositional analysis and electron microscopy imaging is being helpful to further confirm the presence and distribution of such different catalytic materials within the electrodeposits, as well as their composition.

**9th International Symposium on New Materials and Nano-Materials for  
Electrochemical Systems  
XII International Congress of the Mexican Hydrogen Society  
Merida, Mexico, 2012**

## 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 CO<sub>2</sub> 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 (NiMo) system for the HER. This system has demonstrated superior performance [7] and long term stability [8] compared to bare nickel and other nickel alloys, requiring lower overpotentials [7]. In addition, Crespo *et al* [9] showed that NiMo nanoparticles deposited on a glassy carbon electrode presented a current exchange density of  $3.09 \times 10^{-4}$  A/cm<sup>2</sup> compared to  $2.6 \times 10^{-6}$  A/cm<sup>2</sup> for nickel.

## 2. EXPERIMENTAL METHODOLOGIES

The composition of the electrolytic bath used for NiMo alloy deposition contained the following, 0.2M NiSO<sub>4</sub>·6H<sub>2</sub>O (Sigma Aldrich), 0.06M Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O (Mallinckroft Chemical Works), 0.136M Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>·2H<sub>2</sub>O (Baker Analyzed Reagent) and deionized water; the pH was adjusted to 9.0 adding NH<sub>4</sub>OH.

Electrodeposition 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 ( $7 \times 10^{-2}$  cm<sup>2</sup>) and polished with alumina powder with particle diameters of 1, 0.1 and 0.02 μm. 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 Hg/Hg<sub>2</sub>SO<sub>4</sub> electrode (−0.641V vs SHE) and the auxiliary electrode was constructed with a platinum

**9th International Symposium on New Materials and Nano-Materials for  
Electrochemical Systems  
XII International Congress of the Mexican Hydrogen Society  
Merida, Mexico, 2012**

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 were applied in order to deposit the nickel and molybdenum ions from the electrolytic bath; the pulse time was kept constant at 2 seconds in all cases. The current density range used for the electrodeposition experiments was between 7 and 107 mA/cm<sup>2</sup>. Each deposition experiment was performed in triplicate to verify reproducibility of the results. Electrodeposited NiMo alloys were visualized under a FEI scanning electron microscope (Nova Nano SEM 200) and images captured at an accelerating voltage of 15 kV. Quantitative compositional analysis of the deposits was conducted by means of energy dispersive spectrometry (EDAX) integrated to the electron microscope.

Nanoparticle size was quantitatively measured by image analysis (Image J, NIH, Baltimore, MD). Processing of original SEM files consisted of binary image reconstruction at a predetermined grayscale threshold. Approximately 300 in-focus objects were measured to obtain representative determinations of particle size.

The cyclic voltammetry (CV) technique was used to characterize the electrocatalytic activity of NiMo deposits, each electrode was transferred to a 0.78M H<sub>2</sub>SO<sub>4</sub> solution, and a potential sweep from the open circuit potential of the system (usually -0.4V vs Hg/Hg<sub>2</sub>SO<sub>4</sub>) to -0.9V and back to the starting potential was performed. The activity of the deposit was a direct measure of the current generated at a fixed overpotential of 100 mV.

### 3. RESULTS AND DISCUSSION

The polarization potential behavior, the electrochemical characterization, as well as the electrocatalytic activity of fabricated deposits have been previously discussed elsewhere [10], and will be briefly summarized next. Additional work presented here included results on compositional analysis and morphological features of electrodeposits.

Previous results regarding the effect of the applied current density on the polarization potential behavior (Figure 1) suggested that at current densities above 35 mA/cm<sup>2</sup> 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 1 b), where the time is plotted in logarithmic scale. This observation suggests that two different materials were deposited at current densities above 35 mA/cm<sup>2</sup>. The electrochemical characterization of deposits consistently suggested the synthesis of two completely different materials, with distinct electrocatalytic activities for hydrogen evolution. The most active material, whose oxidation potential occurred at -241mV vs Hg/ Hg<sub>2</sub>SO<sub>4</sub>, was named Ia, whereas a second material, showing lower catalytic activity, but higher electrochemical stability than Ia, was referred as IIa. This was found to oxidize at 128mV vs Hg/ Hg<sub>2</sub>SO<sub>4</sub>.

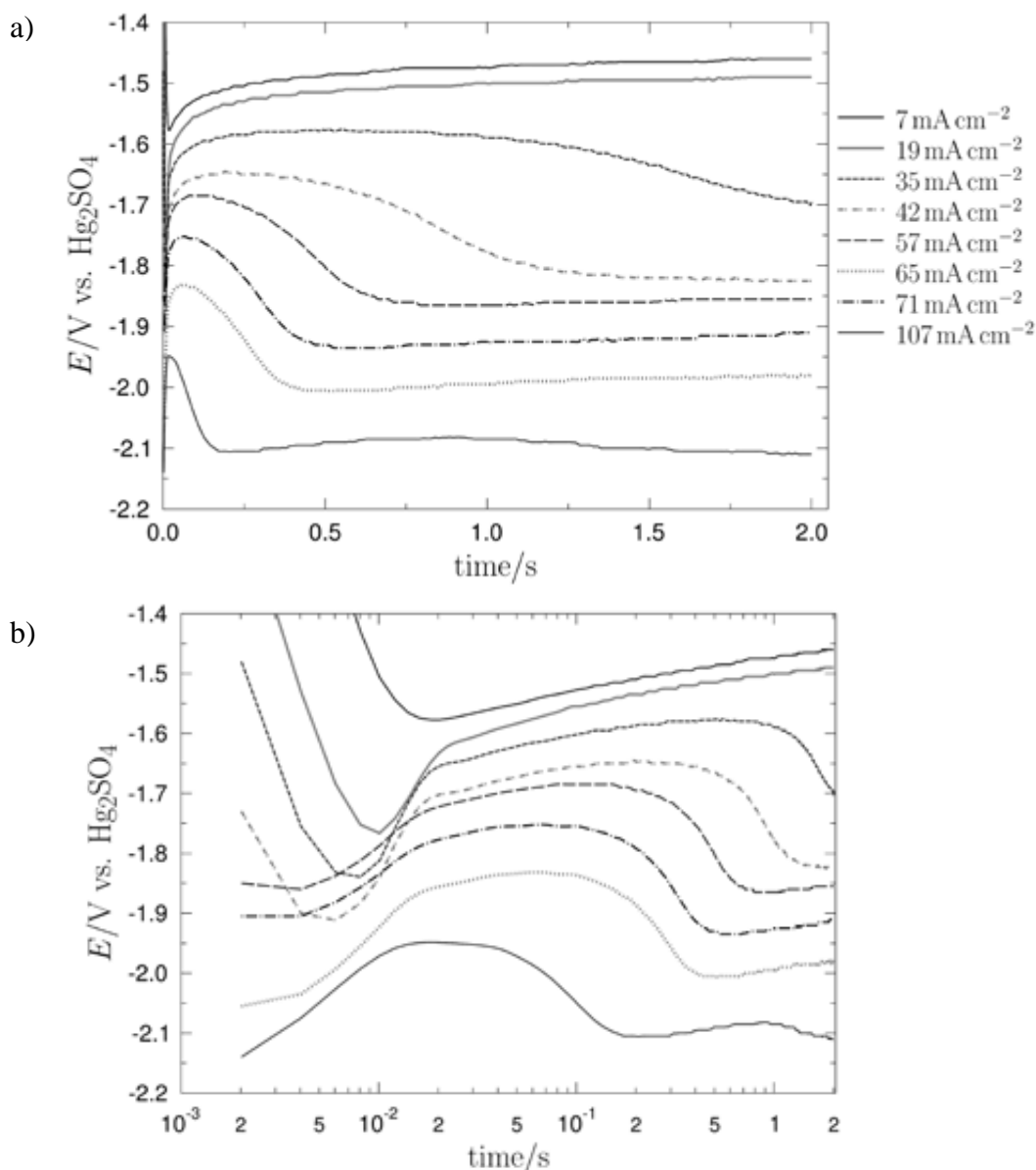


Figure 1. Polarization curves generated upon applying current pulses at different intensities in the range of 7 to 107 mA/cm<sup>2</sup>. The time-axis is in a rectangular (a) and logarithmic (b) scale.

The catalytic activity of electrodeposits for hydrogen evolution was characterized by means of cyclic voltammetry. Figure 2 a) shows voltammograms generated by materials obtained at different current pulsing conditions. The current measured at a given potential is a relative measure of the speed at which hydrogen is being formed on the electrode surface where the NiMo catalyst sits, and therefore of its electrocatalytic activity. Figure 2 b) shows a correlation between the current density used in the preparation of electrodeposits and the current generated at a potential of -0.9V vs Hg/Hg<sub>2</sub>SO<sub>4</sub>. It was 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/cm<sup>2</sup>. The activity of the deposits obtained at currents greater than 100 mA/cm<sup>2</sup> remained practically constant.

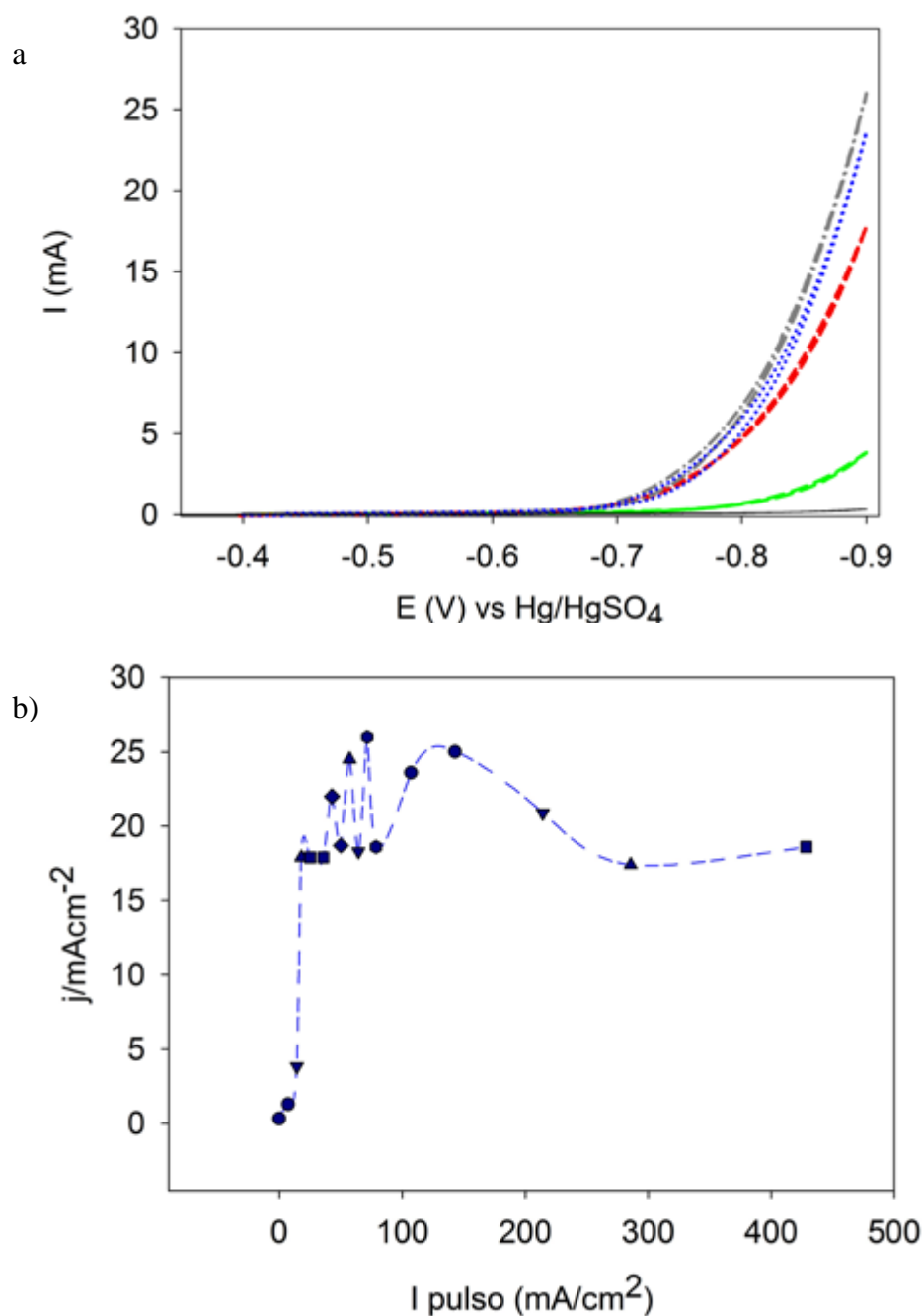


Figure 2. a) Electrocatalytic performance of deposits obtained using current pulses of 25, 35 and 71 mA/cm<sup>2</sup>. b) Current generated -0.9V as function of pulsing current fabrication conditions.

### 3.1. Compositional and morphological characterization of deposits

Figure 3 shows scanning electron microscopy (SEM) images of electrodeposits obtained at an applied current density of 15 mA/cm<sup>2</sup> (a) and b)) and 70 mA/cm<sup>2</sup> (c) and d)). Figures 3 a) and 3 c) were captured at a magnification of 60000X, whereas in Figures 3 b) and 3 d), this parameter was set-up at 120000X. Nanoparticles (NPs) were observed in both cases, *i.e.* at 15 and 70 mA/cm<sup>2</sup>. However higher density (number of nanoparticles per unit area) was found when the applied current pulse was 70 mA/cm<sup>2</sup> in

**9th International Symposium on New Materials and Nano-Materials for  
Electrochemical Systems  
XII International Congress of the Mexican Hydrogen Society  
Merida, Mexico, 2012**

comparison to that observed at  $15 \text{ mA/cm}^2$ . These results were consistent with an expected higher nuclei formation upon increasing the intensity of the current pulse. NP size distributions were obtained by means of quantitative image analysis following the procedure detailed in the Experimental Section. A mean size of 39 and 45 nm was determined when the current pulse was, respectively, 15 and  $70 \text{ mA/cm}^2$ . These results indicate that the influence of the applied current density on the size of nanoparticles was not very significant.

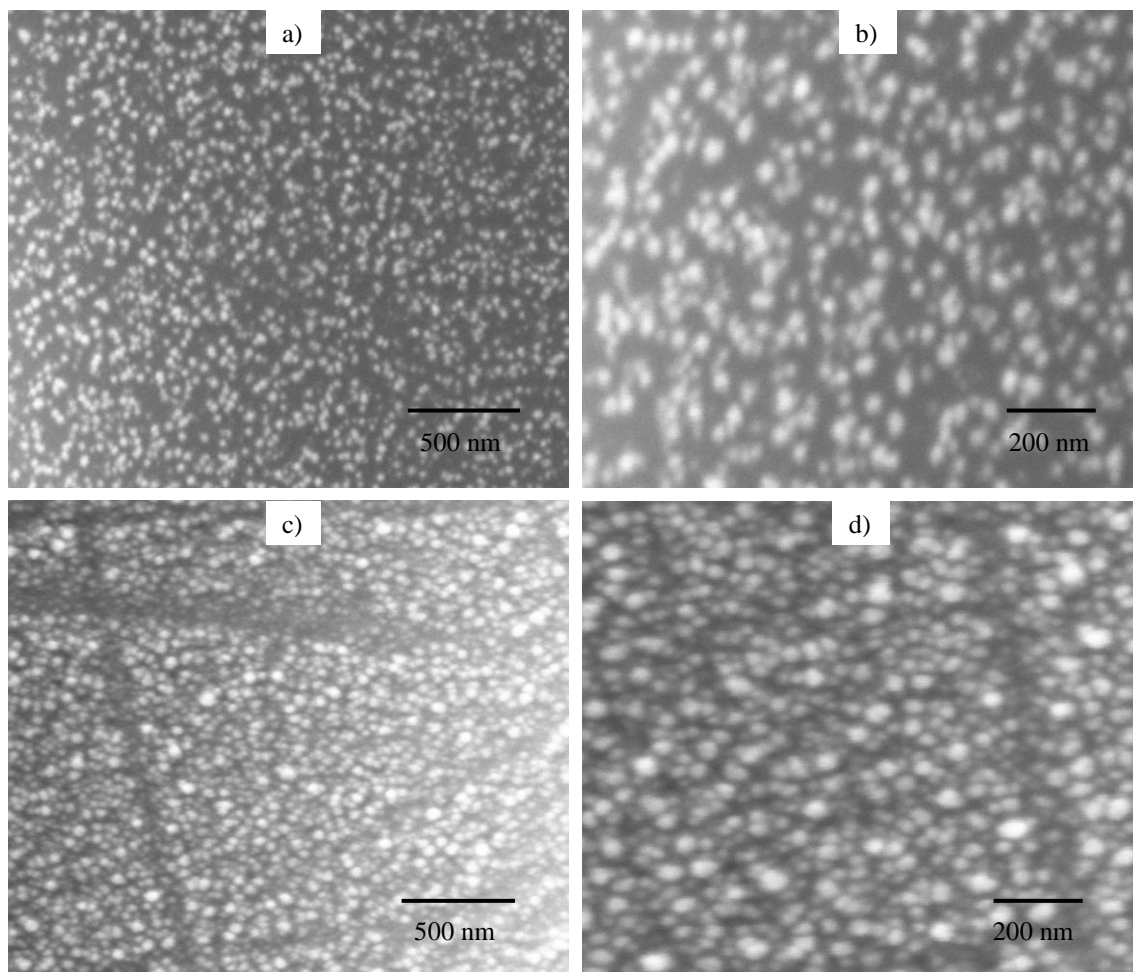


Figure 3. Scanning electron images of electrodeposits fabricated at  $15 \text{ mA/cm}^2$ , a) and b) and  $70 \text{ mA/cm}^2$ , c) and d). The magnification is 60000X in a) and c), and 120000X in b) and d).

In Figure 4, energy dispersive spectrometry (EDXS) results show the compositional analysis of fabricated electrodeposits. The applied current density in Figure 4 a) was  $15 \text{ mA/cm}^2$ , whereas that in Figure 4 b) was  $70 \text{ mA/cm}^2$ . Electrodeposit composition was affected by applied current density; a higher Ni content ( $\sim 4 \text{ wt } \%$ ) observed when the current pulse was  $70 \text{ mA/cm}^2$  contrasted with that determined at  $15 \text{ mA/cm}^2$  ( $\sim 2 \text{ wt } \%$ ). A Mo content of approximately  $0.75 \text{ wt } \%$  was practically unaffected by upon changing the current pulse from 15 to  $70 \text{ mA/cm}^2$ .



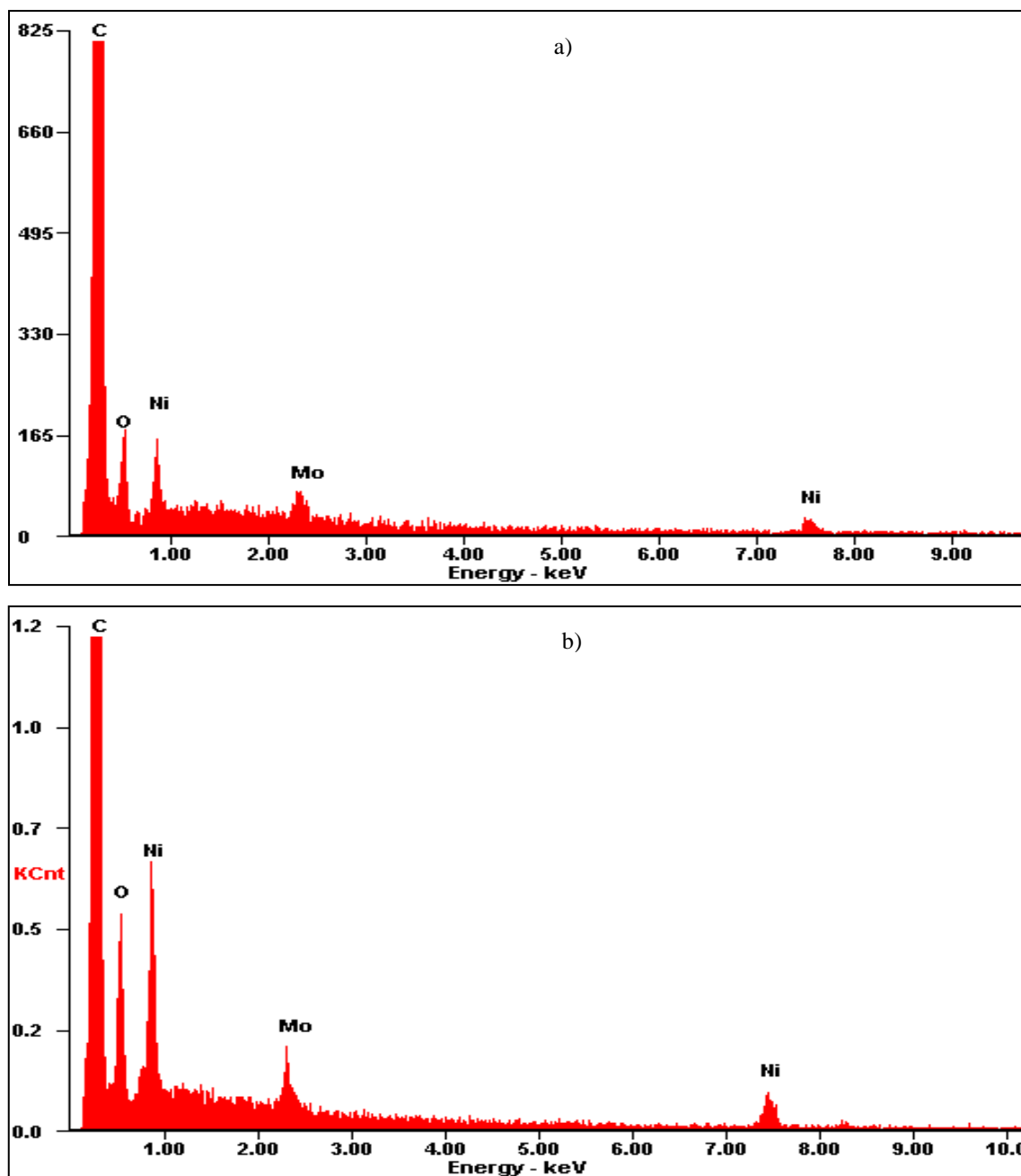


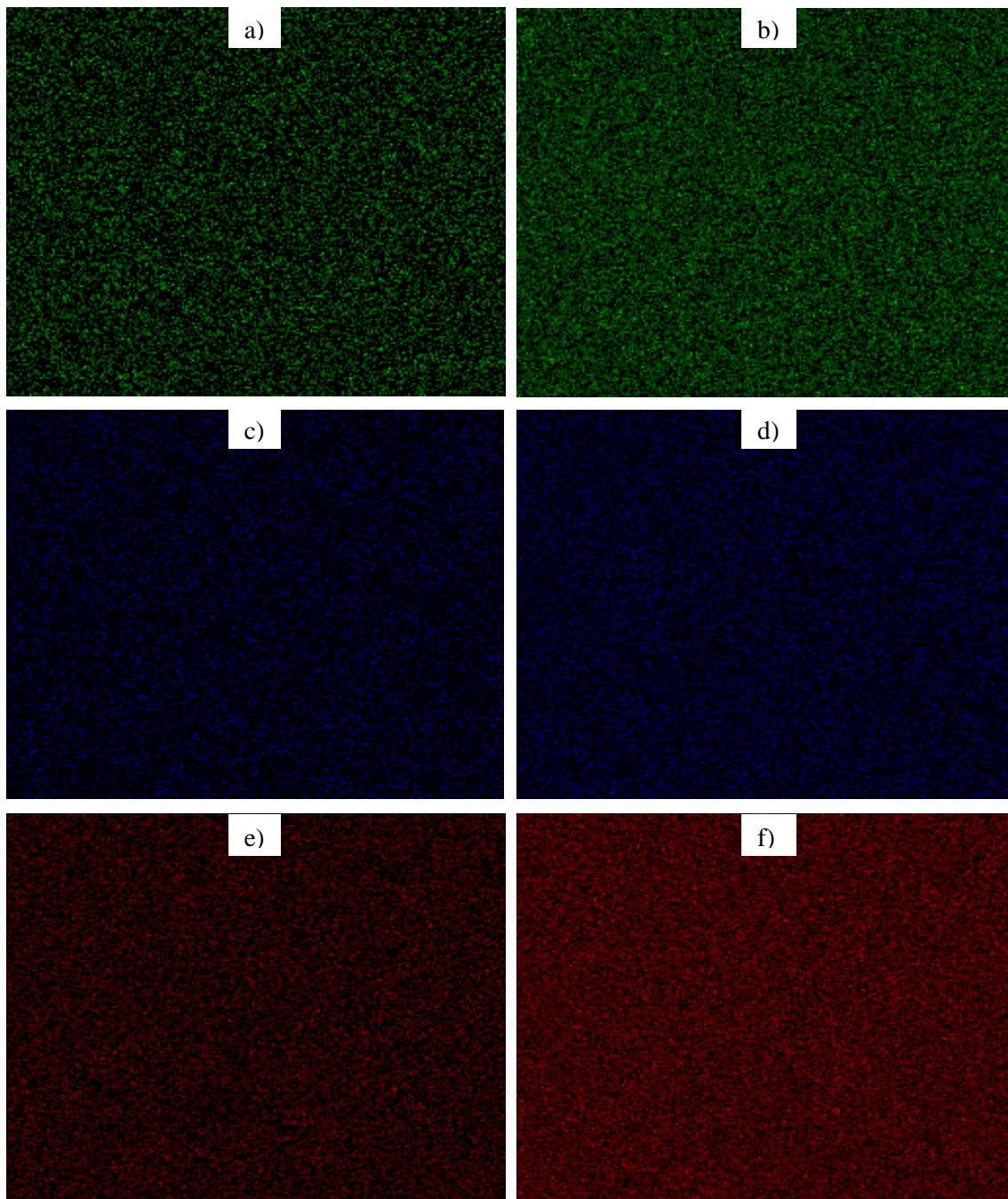
Figure 4. EDXS analysis of electrodeposits fabricated at 15 and 70 mA/cm<sup>2</sup>, a) and b), respectively.

EDXS mapping of deposits shown in Figures 3 a) and 3 c), *i. e.* fabricated at 15 and 70 mA/cm<sup>2</sup>, respectively, are presented in Figure 5. In Figures 5 a), 5 c) and 5 e) the respective detection of Mo, Ni and O within the deposit obtained at 15 mA/cm<sup>2</sup> is presented; Figures 5 b), 5 d) and 5 f) show the distribution of Mo, Ni and O in the deposit fabricated at 70 mA/cm<sup>2</sup>. These results suggested a rather uniform composition of the material throughout the sample, in other words, an approximately identical composition is expected at any point. Additional EDXS analyses of deposits fabricated at different current densities are needed to detect compositional heterogeneities throughout the samples and confirm the possible presence and distribution of two different catalytic materials mentioned above. This work, to be

**9th International Symposium on New Materials and Nano-Materials for  
Electrochemical Systems  
XII International Congress of the Mexican Hydrogen Society  
Merida, Mexico, 2012**

conducted, will be helpful in understanding the role of each material type in the catalytic performance of deposits, as well as the pulsed current conditions at which the deposition of each type is promoted.

The presence of oxygen was evident from EDXS results presented in Figures 4 and 5, and suggested that oxide formation is highly probable. Further EDXS analysis will provide information on the way this oxygen gets incorporated within the electrodeposits, as well as on its role on the catalytic activity of NiMo alloys.





**9th International Symposium on New Materials and Nano-Materials for  
Electrochemical Systems  
XII International Congress of the Mexican Hydrogen Society  
Merida, Mexico, 2012**

Figure 5. EDXS mapping of electrodeposits fabricated at 15 (a), c) and e) and 70 mA/cm<sup>2</sup> (b), d) and f)). Images a) and b) present Mo distribution within the samples, whereas images c) and d) show Ni detection. O distribution is given by images e) and f).

#### 4. CONCLUSIONS

Electrodeposition of NiMo alloys using a binary electrolyte and current pulses showed the formation of nanoparticles ranging in the size of 30 to 50 nm in diameter. The applied current density did not significantly affect nanoparticle size, when changed from 15 to 70 mA/cm<sup>2</sup>. Compositional analysis of deposits indicated a higher Ni content as the intensity of the current pulse was increased; being ~2 wt % at 15 mA/cm<sup>2</sup> and approximately twice as much at 70 mA/cm<sup>2</sup>. Mo content was unaffected upon changing the applied current density from 15 to 70 mA/cm<sup>2</sup>. Electrodeposits showed compositional uniformity at any point within the sample and further studies are needed to confirm the synthesis of distinct types of catalytic materials suggested by the electrochemical characterization of deposits.

#### 5. ACKNOWLEDGEMENTS

The authors acknowledge the financial support provided by CONACyT through the program Colaboración Interamericana de Materiales (No 101939). The research funding from the Tecnológico de Monterrey, Campus Monterrey through the Research Chair in Nanomaterials (CAT120) is also greatly acknowledged.

#### 6. REFERENCES

- [1] N.S. Lewis and D.G. Nocera, PNAS, 103, 15729 (2006).
- [2] F. Hernández, C. Rodríguez, J.L. Hernández, Renewable and sustainable Energy Reviews, 14, 772-780 (2010)
- [3] D. Gust, T.A. Moore, A.L. Moore, Acc. Chem. Res., 42, 1890-1898 (2009).
- [4] W. Hu, Int. J. Hydrogen Energy, 25, 111-118 (2000).
- [5] A. Damian, S. Omanovic, J. Power Sources, 158, 464-476 (2006)
- [6] S. M. Fernández-Valverde, E. Ordoñez-Regil, G. Cabañas-Moreno, O. Solorza-Feria, J. Mex. Chem. Soc., 54(1), 2-6 (2010).
- [7] J. Panek, A. Budnio, Surf. Coat. Tech., 201, 6478-6483 (2006)
- [8] P. Kedzierzawski, D. Oleszak, M. Czachor-Janik, Mat. Sci. Eng. A-Struct., 300, 105-112, (2001).
- [9] M. Videa, D. Crespo, G. Casillas, G. Zavala, J. New Mat. Elec. Syst., 13(3), 239-244, (2010)
- [10] G. Tamayo, Thesis, Chemistry Department, ITESM, Monterrey, Mexico, (2010).

**9th International Symposium on New Materials and Nano-Materials for  
Electrochemical Systems  
XII International Congress of the Mexican Hydrogen Society  
Merida, Mexico, 2012**

[11] G.Tamayo, D. Crespo, M. Videa, in Proceedings of the XI International Hydrogen Congress, Cuernavaca, Mexico, September 20-23, (2011).