

Electrochemical Behavior of Ni-Mo Electrocatalyst for Water Electrolysis

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Abstract. Nickel-molybdenum based electrocatalysts were synthesized in organic media for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) in alkaline media. The structure, morphology, and chemical composition of the catalysts were evaluated by XRD, SEM and AAS. Results revealed nanocrystalline powder materials with Ni_{0.006}Mo, Ni_{0.1}Mo, and NiMo compositions. The best performance for HER, was obtained on Ni_{0.1}Mo electrode, whereas NiMo was for the OER. Results suggest that the material with 1:1 stoichiometric ratio could be considered as a promising electrocatalyst for OER. This nanocrystalline powder is formed by Ni₂Mo₃O₈ and a crystalline structure attributed to the possible formation of a NiMo cluster, becomes NiMoO₄ after thermal treatment at 1073K in air. The NiMo 1:1 cluster catalyst presented electrochemical stability during the OER.

Keywords: NiMo materials, organic chemical synthesis, electrochemical properties, hydrogen evolution reaction, oxygen evolution reaction.

Resumen. Electrocatalizadores base níquel-molibdeno fueron sintetizados en medio orgánico para la reacción de evolución de hidrógeno (HER) y reacción de evolución de oxígeno (OER) en medio alcalino. La estructura, morfología y composición química de los catalizadores fueron evaluados por XRD, SEM y AAS. Los resultados obtenidos mostraron polvos de materiales nanocristalinos con composición química de Ni_{0.006}Mo, Ni_{0.1}Mo y NiMo. El mejor desempeño para la HER fue en electrodos de Ni_{0.1}Mo, y para la OER en NiMo, sugiriendo que el NiMo puede ser considerado como el más prometedor para OER. El NiMo está compuesto de Ni₂Mo₃O₈ y un cluster de NiMo que se transforma en NiMoO₄ después de un tratamiento térmico a 1073K en aire. El catalizador NiMo 1:1 mostró estabilidad electroquímica durante la OER.

Palabras clave: Materiales NiMo, Síntesis química, propiedades electroquímicas, reacción de evolución de hidrógeno, reacción de evolución de oxígeno.

Introduction

The synthesis and characterization of Ni-Mo bimetallic compounds is a very active field of research due its interest in different theoretically and technologically catalytic reactions such as hydrodesulphurization of gas oil [1,2]; dibenzothiophene conversion [3]; and magnetic activities related to their intrinsic properties [4] and also as electrocatalysts for water electrolysis [5,6]. The enhanced activity of an alloy surface is attributed to bifunctional effects in which the unique catalytic properties of each of the elements in the alloy combine in a synergetic manner to yield a surface which is more active than each of the elements alone.

The electrolysis of water is extremely important procedure which has an extensive use in industry for hydrogen generation, where the improved catalytic properties of the electrode materials can act as a beneficial feature of the hydrogen economy [7,8]. The production and use of hydrogen as fuel are a solution to ameliorate the climate change and the environmental problems associated to fossil fuels combustion. Nickel and some of its alloys are among the most attractive industrial electrocatalysts for hydrogen evolution reaction. In alkaline solutions although recent studies of hydrogen evolution in acidic media [9] pointed out NiMo as a prominent electrocatalyst for this cathodic reaction. Nickel is up to now the most used elec-

trocatalyst in commercial alkaline electrolyzers and has been considered a reference electrode against some other evaluated materials. Oxygen evolution reaction is also an important process in water electrolysis [10] and in some anodic reactions on molecular organic electrochemistry. Nickel oxides (NiO) have also been reported as prominent electrocatalysts for oxygen evolution reaction in alkaline solution [11,12]. A reported proper combination of a large surface area with an enhanced catalytic activity can be produced by co-deposition of nickel with metals such as cobalt (Co) [13], molybdenum (Mo) [14] and phosphorus (P) [15]. A study of Ni-Mo-P alloy and Ni-Mo materials are also reported in the literature for oxygen evolution [16, 17]. The investigation on the synthesis, electrical and optical characterization of novel materials fabricated at low temperature has increased. Electrodeposition, sol-gel, and chemical route deposition are among the most common used techniques for Ni-Mo compound preparations [15,18-21] although the decomposition of molybdenum carbonyl Mo(Co)₆ over nickel has been reported in the synthesis of Ni-Mo alloys [22]. The aim of this work was to develop the synthesis and characterization of a NiMo based electrocatalysts produced by reacting molybdenum carbonyl with nickel compounds in organic media. The electrochemical performance of these electrocatalysts as electrodes for water electrolysis in alkaline media is reported.

Results and discussion

Chemical composition. The chemical composition of sample A, synthesized by reacting the transition carbonyls $\text{Ni}(\text{CO})_6$ with $\text{Mo}(\text{CO})_6$, was $\text{Ni}_{0.006}\text{Mo}$, thought to be a nickel-doped-molybdenum compound. The amount of nickel was increased in sample B, with a formula $\text{Ni}_{0.1}\text{Mo}$ and, only in sample C a stoichiometric ratio NiMo was obtained. From the quantified amounts of nickel and molybdenum, a lack of approximately 30 weight per cent was observed; this could be attributed to the presence of bridge carbonyls in some Ni-Mo clusters of different nuclearities produced during the synthesis process.

X-ray diffraction analysis and SEM morphology. Figures 1 and 2 show X-ray diffraction spectra of samples B and C, respectively. In both cases, amorphous behavior was observed at short times of spectra. In sample B, metallic nickel was found (JPCDS card 4-580) and in sample C, a slight quantity of a nanocrystalline compound was observed, the reported diffraction spectra (figure 2) was taken for 24 h., The highest refractions corresponds to atomic distances of 5.46, 4.79, and 2.91 Å. These values are not related to nickel carbonate (JPCDS card 00-10-0272) starting material neither to NiO , molybdenum oxides (MoO_3), or NiMo alloys reported in JPCDS cards but the distance. In figure 2 the refractions

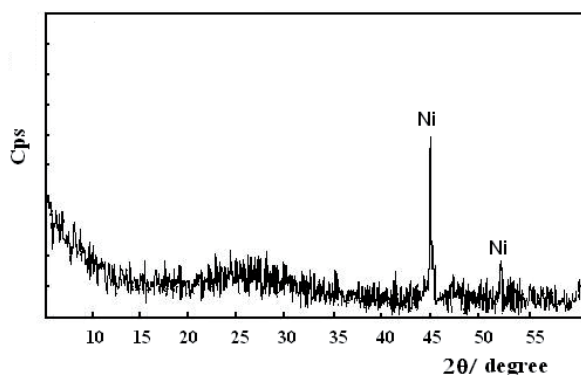


Fig. 1. X-ray diffraction spectrum of $\text{Ni}_{0.1}\text{Mo}$ synthesized from Ni and $\text{Mo}(\text{CO})_6$ in 1,2 dichlorobenzene.

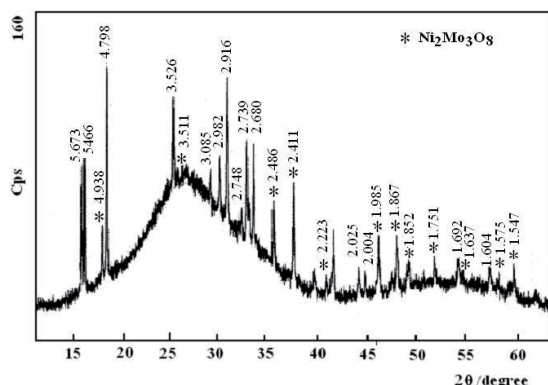


Fig. 2. X-ray diffraction spectrum of NiMo synthesized from NiCO_3 and $\text{Mo}(\text{CO})_6$ in 1,2 dichlorobenzene. (numbers in figure corresponds to distances in Å°).

signaled with an (*) corresponds to $\text{Ni}_2\text{Mo}_3\text{O}_8$ (JPCDS card 00-037-0855). The rest of the spectra involve also lower and higher nuclearity cluster compounds as reported before in the synthesis of WRuSe clusters in organic media [20] and MoOsSe cluster carbonyl [30] compounds. To get more information about this compound, the powder was thermally treated four hours at 1073 K, and the X-ray spectra obtained is depicted in figure 3. The synthesized NiMo powder material does not corresponds to NiMoO_4 , (JPCDS card 33-0948) [23] and,

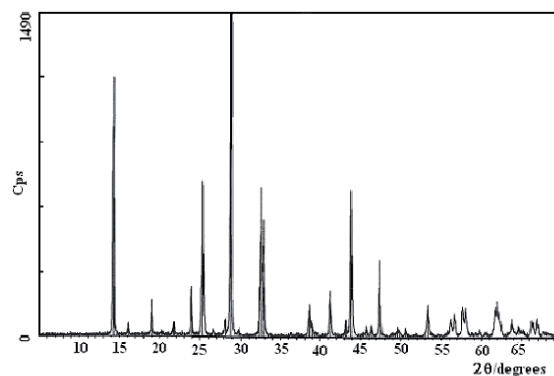


Fig. 3. X-ray diffraction spectrum of NiMo , heated for 2 hours at 1073 K. The marked lines correspond to NiMoO_4 .

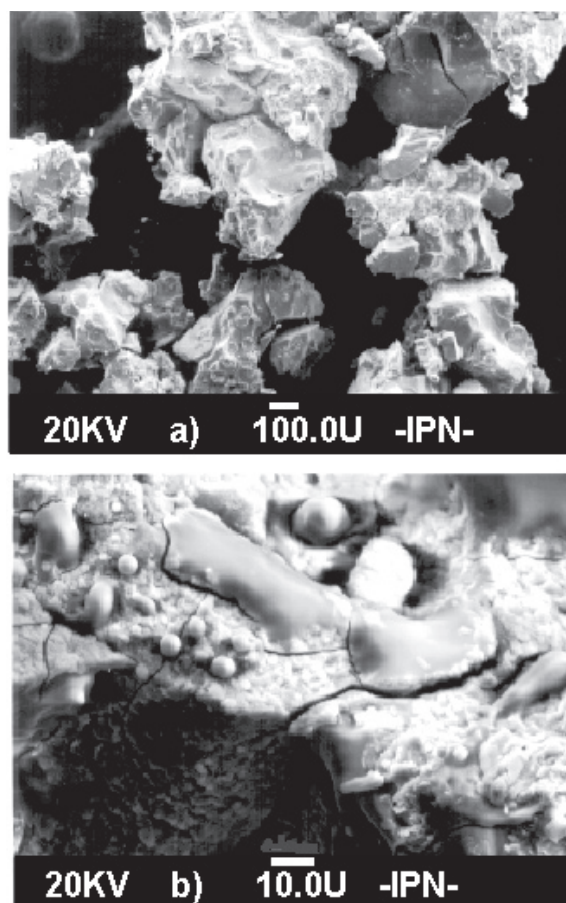


Fig. 4. SEM image of $\text{Ni}_{0.1}\text{Mo}$ synthesized from Ni and $\text{Mo}(\text{CO})_6$ in 1,2 dichlorobenzene.

don't have any diffraction peaks corresponding to $\text{Ni}_2(\text{MoO}_4)_3$ reported in figure 2 of R.S. Prabhakaren *et al.* article [24].

Figure 4 shows the SEM micrograph of $\text{Ni}_{0.1}\text{Mo}$ synthesized from metallic nickel and molybdenum carbonyl. In Figure 4a) particles larger than $24\ \mu\text{m}$ are observed, showing a cracked morphology. The chemical analysis of this material was performed in situ and the flat and smooth surface shown in Figure 4b), corresponds to metallic nickel; the grains to a NiMo compound and the rough surface correspond to an enriched molybdenum phase. Figure 5 shows the morphology of NiMo prepared from NiCO_3 and $\text{Mo}(\text{CO})_6$. The surface of NiMo has a spongy form with agglomerated particles less than $1\ \mu\text{m}$.

Roughness factor. The roughness factor, defined as the electrochemical surface area, was determined by scanning the materials in three different potential regions where non-

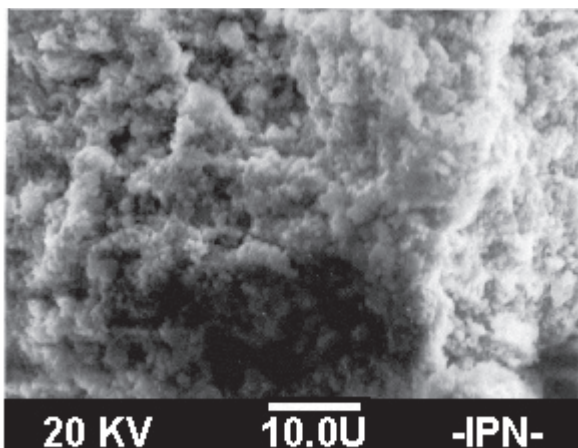


Fig. 5. SEM image of NiMo synthesized from NiCO_3 and $\text{Mo}(\text{CO})_6$ in 1,2 dichlorobenzene.

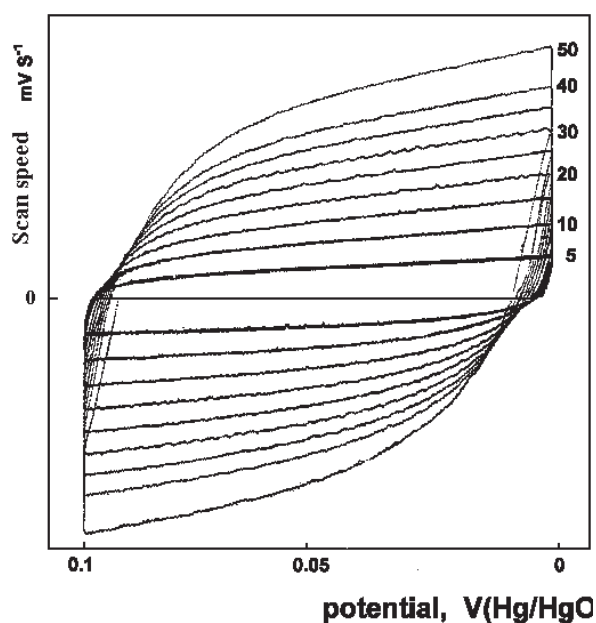


Fig. 6. Cyclic voltammograms of the NiMo electrode in the potential region of 0.0-0.1 V, at various scan rates in 0.5M KOH at 291 K.

faradaic reactions were observed. The voltammograms for NiMo electrode in the region of 0 to $-0.100\ \text{V}$ (Hg/HgO) are shown in Figure 6. The capacitance charging current densities were measured at the middle of the scan range and the double layer capacitance calculated from the slope of the linear part of the charging current density against the scan rate. The roughness factor was estimated by considering the relation given by Levine and Smith [25] of the double layer capacitance for smooth surface in the region of chemisorbed oxygen layer on polycrystalline electrodes, taking into account that the contribution of the carbon in the double layer capacitance is the same in both electrodes. The determined roughness factors were 54.6 and 55.7 for the $\text{Ni}_{0.1}\text{Mo}$ and NiMo, respectively.

Electrochemical behavior. Figures 7 to 9 show cyclic voltammograms in 0.5M KOH at 291K of $\text{Ni}_{0.006}\text{Mo}$, $\text{Ni}_{0.1}\text{Mo}$, and NiMo, respectively, in regions for hydrogen and oxygen evolution reactions. The voltammograms for hydrogen evolution were recorded between 0.0 and $-1.30\ \text{V}$ (Hg/HgO) with a potential scan rate of $50\ \text{mV s}^{-1}$ as shown in Figures. 7a-c. The shape of the curves shows a direct cathodic electron transfer reaction. The values of current density deduced from Figure 7 at $-1.30\ \text{V}$ (Hg/HgO) are given in Table 1, taking into account the geometric surface area of each electrode. These electrochemical results demonstrate that for hydrogen evolution reaction, these materials presents relatively poor activity compared

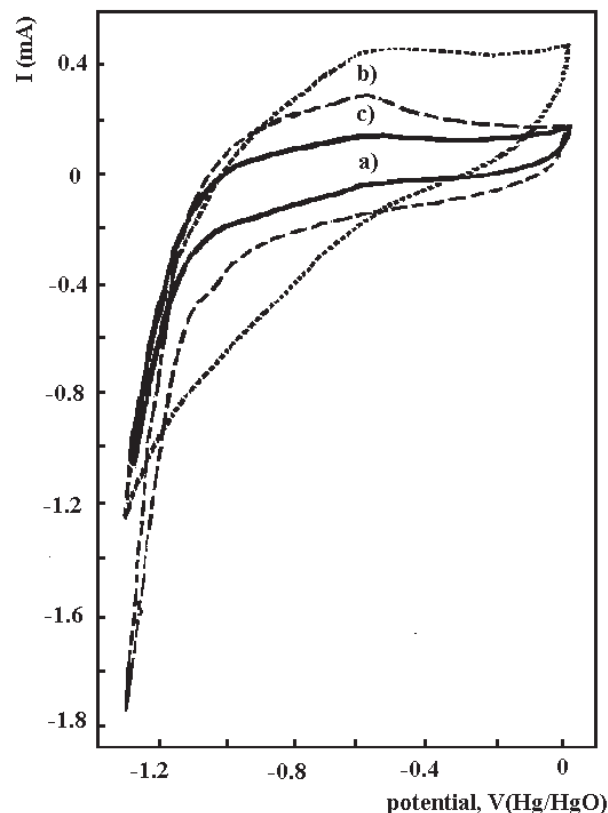


Fig. 7. Cyclic voltammograms for hydrogen evolution reaction by a) $\text{Ni}_{0.006}\text{Mo}$; b) $\text{Ni}_{0.1}\text{Mo}$ and c) NiMo in 0.5M KOH at $50\ \text{mV s}^{-1}$.

Table 1. Current Density (mAcm^{-2}) for hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) for samples of Ni-Mo electrodes at different electrode potentials in 0.5 M KOH solution.

Sample	HER(-1.3 V)	OER(0.70 V)	OER(1.0 V)
$\text{Ni}_{0.006}\text{Mo}$	5.5	1.5	24.5
$\text{Ni}_{0.1}\text{Mo}$	6.9	2.7	12.2
NiMo	6.4	12.1	31.8
NiMo Δ	9.5	10.0	66

with other reported results for Ni-Mo alloys, obtained by different techniques [26,27,]. This behavior is attributed to the amorphous component surrounding the alloy. However, after annealing of NiMo at 473K for 2 hours, the electrochemical behavior for the cathodic reaction was assessed obtaining a decreased value comparable to that obtained with $\text{Ni}_{0.006}\text{Mo}$. A more detailed study is required to evaluate the real catalytic activity taking into account not only the kinetic parameters but also the overpotential of each catalyst at a fixed current density under steady state conditions.

The same catalysts were tested in the region of the oxygen evolution reaction. Figures 8a-c show polarization results of these materials tested in the region of 0.0-1.00 V (Hg/HgO) under the same experimental condition, as reported for the oxygen evolution reaction. Values of current densities at 0.70 V vs. (Hg/HgO) obtained for $\text{Ni}_{0.006}\text{Mo}$, $\text{Ni}_{0.1}\text{Mo}$, and NiMo, are given in Table 1. Scanning the electrode potential to a more anodic value, the current density increased with the applied potential, as can be seen in Figures 8a-c; in the case of the NiMo, a current density of 31.8 mAcm^{-2} at 1V (scan rate 20 mVs^{-1}) was attained. The electrochemical result obtained with this material was higher compared with other reported

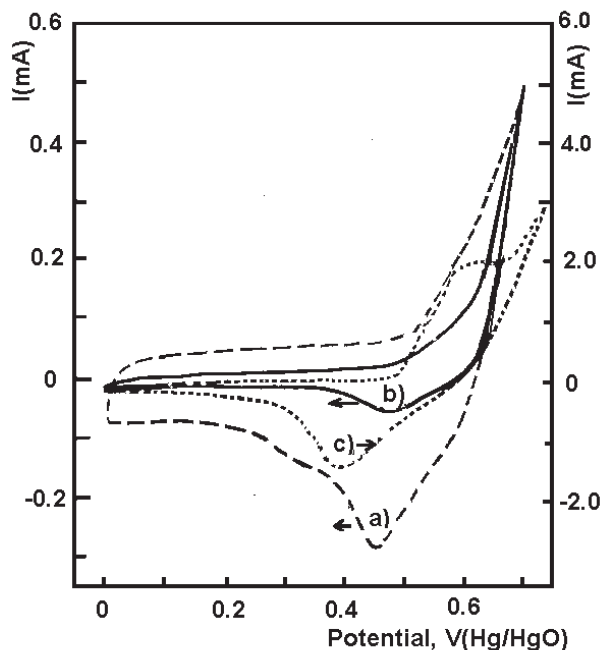


Fig. 8. Cyclic voltammograms for oxygen evolution reaction by a) $\text{Ni}_{0.006}\text{Mo}$; b) $\text{Ni}_{0.1}\text{Mo}$; c) NiMo in 0.5M KOH at 50 mVs^{-1} .

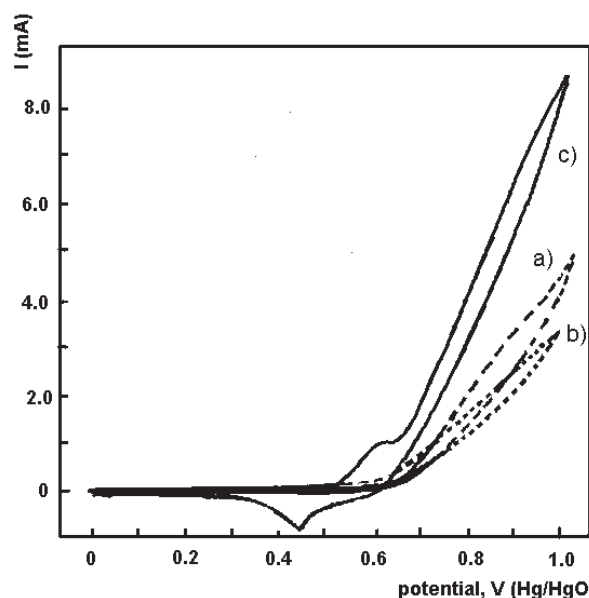


Fig. 9. Cyclic voltammograms for oxygen evolution reaction by a) $\text{Ni}_{0.006}\text{Mo}$; b) $\text{Ni}_{0.1}\text{Mo}$; c) NiMo in 0.5M KOH at 20 mVs^{-1} .

electrocatalysts such as Co_3O_4 , synthesized by sol-gel and tested for the same reaction under the same condition, i.e. 25 mAcm^{-2} [28]. To date, our result for oxygen evolution in the NiMo is better than that reported for Ni/NiCo $_2$ O $_4$, i.e., 6 mA cm^{-2} at 600 mV [figure 2b in reference 12] and with the same magnitude of that obtained for the same material reported by Suffredini et al [29]. As the roughness factor is almost the same in $\text{Ni}_{0.1}\text{Mo}$ and NiMo, the difference in electrochemical activity could not be attributed to the roughness factor as has been reported in other materials such as Co_3O_4 obtained by different techniques [28], but rather to the intrinsic properties of $\text{Ni}_{0.1}\text{Mo}$ and NiMo, related to the geometric and electronic configurations. The thermally treated NiMo compound has a decreased electrocatalytic activity for the oxygen evolution reaction compared to that of NiMo at 0.7 V, but it is increased at 1 V, such as observed in table 1. The difference between the as obtained and thermally treated material could be attributed to a geometric structure modification of the cluster catalyst in the substitution of some molybdenum carbonyl bonds by molybdenum oxygen bonds formed by heating the compound in air or to the surface cleaning of some organic material, coming from the synthesis.

Electrochemical stability Figure 10 shows prolonged chronoamperometric experiments performed in the alkaline solution in order to explore the stability of $\text{Ni}_{0.1}\text{Mo}$, NiMo, and MoO_3 (Aldrich reactive grade) for the oxygen evolution reaction. These curves were obtained at 0.75 V (Hg/HgO), for 24 hours. $\text{Ni}_{0.1}\text{Mo}$ shows almost the same behavior as MoO_3 , confirming our advanced conclusions of the formation of a nickel-doped-molybdenum compound in the experimental conditions the molybdenum is dissolved in the electrolyte. These materials are not stable as electrodes for the oxygen evolution reaction. Whereas NiMo has a good stability for oxygen evolution as shown in Figure 11, however, there exists

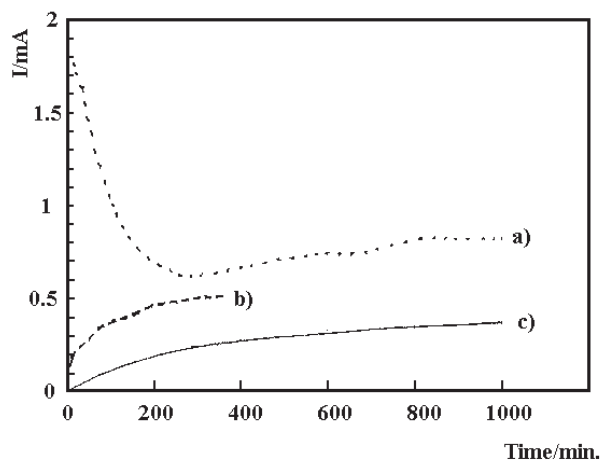


Fig. 10. Stability under potentiostatic polarization at 0.75 V/(Hg/HgO) for a) NiMo, b) Ni_{0.1}Mo; c) MoO₃.

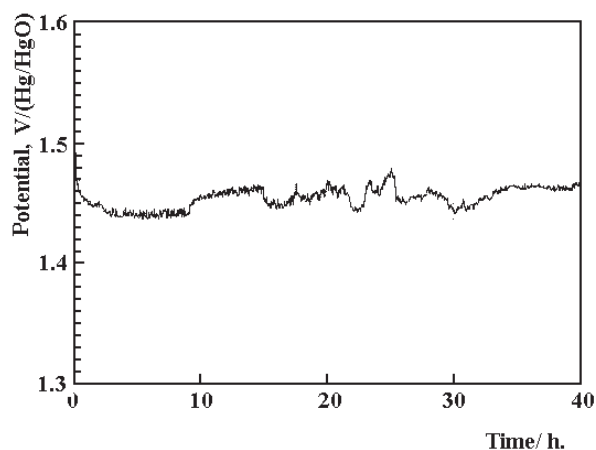


Fig. 11. Galvanostatic polarization for NiMo at $I = 1.5$ mA at 291K.

a possibility of CO₂ formation during the oxygen evolution because carbon has been used as catalysts support. The NiMo stability confirms that Ni₂Mo₃O₈ and the other compounds not determined in this work are stable for the oxygen evolution reaction. These results suggest the unidentified part of NiMo must be cluster compound formed in the organic media as has been reported for ruthenium base and osmium base electrocatalyst [19-21, 30, 31] obtained under the same experimental conditions. For the other peaks any isomorphic compound was found in the X-ray data spectra of the diffractometer or in the literature.

Conclusion

Ni-Mo electrocatalyst synthesized from different nickel reagents in 1,2 dichlorobenzene present activity for hydrogen evolution in alkaline solution. XRD spectra shows the formation of a NiMo crystalline compound in nanometric size and, formed by Ni₂Mo₃O₈ and other non identified cluster compounds. The best results for the oxygen evolution reaction were obtained after annealing the NiMo sample at 473K. The

chemical synthesis route allows the preparation of a Ni-Mo material stable for oxygen evolution reaction and materials with high active surface area in relation to that obtained by sol-gel or spray-pyrolysis. In these materials, the difference in electrocatalytic activity could not be attributed to the roughness factor, but rather to their intrinsic properties. The hydrogen evolution reaction is poor compared with other reported results for Ni-Mo alloys.

Experimental

Ni-Mo oxides were prepared following a procedure similar to that previously reported for ternary ruthenium-base electrocatalysts [19-21], by reacting molybdenum carbonyl Mo(CO)₆ (Strem) and nickel carbonyl compound, Ni(CO)₄ (Strem), in 1,2 dichlorobenzene (Merck) under a refluxing condition (bp~ 453K); or nickel powder (Merck) and Mo(CO)₆; or NiCO₃ (Baker) and Mo(CO)₆, all of them under the same experimental conditions. Before and during the synthesis, the organic solvent was outgassed with dry nitrogen. The Mo(CO)₆ was dissolved in 100 mL of freshly distilled 1,2 dichlorobenzene; the organic solvent was heated to boiling point; afterward, Ni(CO)₄ gas was bubbled through the solution for 15 min. After 20 h of reaction, the products were centrifuged and the recuperated black powder was washed with diethyl ether and dried at room temperature (sample A). Sample B was obtained by reacting 0.05 mmolL⁻¹ of nickel powder with 0.57 mmolL⁻¹ of Mo(CO)₆ in 100 mL of dichlorobenzene. Sample C was prepared by reacting 1.14 mmolL⁻¹ Mo(CO)₆ with 0.84 mmolL⁻¹ NiCO₃ in 100 mL of dichlorobenzene for 20 h, following the same experimental procedure.

The chemical analysis of the samples was done in a Perkin-Elmer Atomic Absorption Spectrophotometer (Mod. 2380), determining the weight percent composition of nickel from air acetylene flame and molybdenum from a nitrous oxide acetylene flame. The X-ray spectra were performed in a Siemens X-ray diffractometer using the Cu-K α radiation. The morphology of the samples was examined by a scanning electron microscope, JEOL (JSM-35CF).

A standard electrochemical setup was used for current-potential measurements. Working electrodes were prepared by mixing samples in powder form with a previously prepared carbon paste and placed in a cup of an electrode holder made of nylamid with a stainless steel contact at the bottom [19, 21]. The geometrical surface area of each electrode was 0.19 cm² for Ni_{0.006}Mo and Ni_{0.1}Mo and 0.28 cm² for NiMo which were smoothed by rubbing gently on pieces of weighing paper. The reference electrode was Hg/HgO/OH⁻ in 0.5M KOH and a Pt grid was used as the auxiliary electrode. The solutions were prepared with KOH (Merck) and distilled water. All the experiments were developed in 0.5M KOH at 291K. The electrochemical measurements were performed with a Potentiostat-Galvanostat (EG&G, Princeton Applied Research, Mod. 273A), connected to a Hewlett-Packard X-Y recorder Mod. 7004).

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