Electrochemical and morphological studies of electrodeposited Ni–Fe–Mo–Zn alloys tailored for water electrolysis

F.C. Crnkovic, S.A.S. Machado, L.A. Avaca

Dept. de Fisico-Quimica, Instituto de Quimica de Sao Carlos, Universidade de Sao Paulo, C.P. 780, 13560-970 Sao Carlos, SP, Brazil

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Abstract

The co-deposition of nickel, iron and molybdenum onto mild steel substrates with or without the addition and subsequent leaching of zinc rendered cathode materials very active for hydrogen generation in alkaline solutions. SEM analysis showed that adherence to the substrate can be achieved by initial deposition of the other components prior to Zn incorporation into the solution. Coatings of Ni–Fe–Mo (51.4-5.5-43.1 at%) and Ni–Fe–Mo–(Zn) (70.9-15.3-12.7-1.1 at% after leaching) were very active for hydrogen evolution at temperatures ranging from 25 to 80°C in 6 M KOH solutions. Steady-state polarisation curves furnished Tafel plots with slopes almost invariant with temperature and revealed an electrochemical activity comparable to the best materials reported so far. For the Ni–Fe–Mo–(Zn) coating the overpotential for hydrogen evolution at 80°C was as low as 83 mV. Long-time electrolyses at a constant current density of 135 mA cm⁻² showed a considerable degradation of the surface and a decay in performance but the overpotential value after 440 h stabilised in 157 mV, a satisfactory value for industrial applications.

Keywords: Co-deposition; Cathode materials; Hydrogen evolution; Ni-based alloys; Molybdenum

1. Introduction

The development of novel materials with low overpotential towards the hydrogen evolution reaction (HER) could be based on the use of two complementary characteristics of electrodeposits, namely, intrinsic catalytic activity and high surface area [1,2]. Aiming to explore the former characteristic, several studies on Ni–Fe–Mo alloys have been published. In this way, the catalytic activity of Ni–Mo–Fe for hydrogen cathodes was analysed in a laboratory size electrolytic cell with the electrode working at 1.8 V, 300 mA cm⁻² in 6 M KOH, with long term operation [3]. The activity of Ni–Mo–Fe alloy electrodeposited on mild steel electrode for the hydrogen evolution reaction (HER) was compared with several other ternary Ni composites like Ni–Mo–Cu, Ni–Mo–Zn, Ni–Mo–Co, Ni–Mo–W and Ni–Mo–Cr. The authors reported that the best and most stable hydrogen evolving cathode was Ni–Mo–Fe, which exhibited an overpotential about 0.187 V for over 1500 h of continuous electrolysis in 6 M KOH at 300 mA cm⁻² and 353 K [4,5]. Amorphous Ni–Fe–Mo alloys obtained by electrodeposition from an alkaline citrate bath were also evaluated towards their activities for the HER in 30 wt% KOH at 70°C [6]. The results showed that Ni₄₁.₄⁹Fe₂₃.₀₂Mo₃₅.₄⁹ alloy presented the best activity for HER presenting an overpotential of approximately 100 mV for an applied current density of 200 mA cm⁻², the electrode were found to be stable for 1200 h of continuous operation. Even when current interruptions were imposed to the electrode, the stability remained the same, thus indicating that Ni₄₁.₄⁹Fe₂₃.₀₂Mo₃₅.₄⁹ alloy is resistant to corrosion in hot KOH medium [6]. Electrolytic Ni–Fe–Mo alloy has also been obtained from sulphate bath and investigations regarding its morphology and catalytic activities were performed [7]. The alloy showed good stability for electrolysis in 30% KOH at 100 mA cm⁻² and 343 K, presenting an overpotential of approximately 120 mV. On the other hand,
aiming to associate the good catalytic activity of Ni–Fe–Mo coatings with the advantage of large surface areas, previous studies [8–14] have shown that the incorporation of Zn into Ni and Ni–Co deposits and subsequent alkaline leaching of the superficial Zn leads to large area structures with enhanced activity for the her. Additionally, Ni–Fe coatings properly pre-activated by anodic oxidation [9] are also very active cathodes. However, early attempts made in our laboratories to deposit such alloy on large area Ni or Ni–Co substrates failed to provide a material more active than the substrate itself. On the other hand, it has been recently reported that the incorporation of Mo into Ni–Fe alloys furnishes a material with high activity for the her [15,16].

The aim of this work was the preparation, physical characterisation and electrochemical behaviour in alkaline solutions of Ni-based alloys that efficiently combine the two properties described above. In particular, Ni–Fe–Mo and Ni–Fe–Mo–(Zn) co-deposits on mild steel substrates have been prepared and pre-treated in a variety of ways to maximise their performance as cathode materials in strong basic media.

2. Experimental

2.1. Electrodeposition of alloys

Electrodeposition of the alloys was carried out onto 6 mm mild steel rods embedded in epoxy resin and polished to expose a 0.28 cm² flat disk. The plating bath and conditions [9] were used for the following coatings: (1) Ni–Fe–Mo: 64 g/l NiSO₄·6H₂O + 10 g/l Na₂MoO₄·2H₂O + 16 g/l FeSO₄·7H₂O + 53 g/l Na₃C₆H₅O₇·2H₂O + 75 g/l Na₂CO₃ + H₂SO₄ (pH = 0.5), at 30°C and 40 mA cm⁻² for 100 min.; (2) Ni–Fe–Mo–(Zn): same conditions and bath as (1) but with the addition of 5 g/l ZnSO₄·7H₂O either at beginning of the deposition (type-a deposits) or after plating for 60 min. (type-b deposits). In later case, leaching of the Zn was performed by immersion in 28% KOH solution at 80°C for 4 h and the two treated samples named as type-a* and type-b*, respectively.

2.2. Physical characterisation and electrochemical measurements

Surface composition, morphology and thickness of the three samples were analysed by energy dispersive X-Ray analysis (EDX) in a link analytical QX 2000 microanalyser, atomic force microscopy (AFM) using a topometrix TMX 1010 Explorer instrument and scanning electron microscopy (SEM) in a Zeiss DSM 960 apparatus. The thickness was estimated by lateral observation of the samples deposited on Cu substrates.

The electrochemical measurements were carried out in a three compartment cell using an EG&G PARC mod. 273 potentiostat having ohmic drop compensation by the current interrupt method and linked to a microcomputer. The auxiliary electrode was a 5 cm² Ni plate while the reference electrode was an Hg/HgO/OH⁻ electrode in the same electrolyte. All solutions were prepared with P.A. chemicals and water purified by a Milli-Q system. A 6 M KOH solution was used as electrolyte.

3. Results and discussion

Fig. 1 shows the SEM images of the three samples. In all cases, the surface is of globular nature not showing the features that are usually associated to Zn-containing deposits [9]. Lateral observation of the coatings reveals a good adhesion to the substrate except for the type-a* Ni–Fe–Mo–(Zn) deposit. This indicates that the delayed addition of the zinc salt to the plating bath (see Experimental section) is a proper procedure to avoid disintegration of the coating during the alkaline leaching or even during continuous operation in strong basic media.

Morphological observation of the electrode surfaces was also carried out by AFM analyses recorded in the contact mode. The images for the Ni–Fe–Mo coating as prepared and for the type-b* Ni–Fe–Mo–(Zn) after alkaline leaching are presented in Fig. 2 together with illustrative profiles recorded across the samples.

Two interesting features emerge from those images. Firstly, the profiles recorded for the two materials clearly indicate that the surface roughness of the deposit initially containing Zn is higher than the other. This suggests an increased activity for the her even in the case of similar bulk compositions. Secondly, the co-deposition of Zn is not large or efficient enough to produce very high surface areas, as previously reported [9]. This means that further improvements in the electrode performance can be achieved by optimisation of that step.

The surface composition of the coatings was determined by EDX analysis and compared with that of the plating solution. The values are collected in Table 1 and clearly show a great enhancement of the Mo concentration in all cases after plating. Meanwhile, for the Zn-containing coatings this discrepancy practically disappears after alkaline leaching. This suggests that the Mo is temporarily incorporated to the surface, perhaps as a consequence of a partial oxidation to Mo(III) and subsequent precipitation as an hydroxide. The hot alkaline leaching (at 50°C for 2 h) removes this species and the composition of the coatings becomes very close to that of the plating solution.

Steady-state polarisation curves for the her were recorded galvanostatically in 6 M KOH at different temperatures. The overpotential values were corrected for ohmic drop by the current interrupt method. Fig. 3 shows a comparison among three cathodes and bright Ni at 25°C. The enhanced activities of all Ni–Fe–Mo–(Zn) coatings, compared with the Ni
Fig. 1. SEM images of the as-prepared Ni–Fe–Mo and two types (a* and b*) of Ni–Fe–Mo–(Zn) after alkaline leaching.

one, are showed by the much smaller value for the hydrogen overpotentials observed. Among the cathodes under study, the (type-b*) Ni–Fe–Mo–(Zn) is the most active, with an overpotential of nearly 0.09 V at 100 mA cm$^{-2}$ and 25°C. Fig. 4 illustrate the general behaviour of (type-b*) Ni–Fe–Mo–(Zn) coatings after hot alkaline leaching, at the several temperatures indicated in that figure.

As it is clear from the previous Figs. 3 and 4, the introduction of Mo considerably improves the cathodes performance in comparison to bright Ni. Furthermore, the incorporation and later removal of Zn from the coating renders materials very active for the her.

The complete set of electrochemical parameters for the her on Ni–Fe–Mo and (type-b*) Ni–Fe–Mo–(Zn) at different temperatures is presented in Table 2, where the value of $\eta_{135}$ (overpotential corresponding to a current density of 135 mA cm$^{-2}$) is also included for a performance comparison in a region unaffected by ohmic drop. The corresponding results for (type-a*) Ni–Fe–Mo–(Zn) were excluded since that coating does not show an adequate electrochemical stability and suffers disintegration during operation.

It could be noticed from Table 2 that the values of the Tafel slope are very low in both cases and do not follow a proper dependence with temperature. This phenomenon has already been observed for Ni and Ni–Co active coatings [8] and is probably due to the interference of absorbed hydrogen into the Ni matrix when the cathodic reaction is occurring at low current densities.

Regarding the electrochemical activity of the coatings towards the her, the (type-b*) Ni–Fe–Mo–(Zn) shows an overpotential value of 83.1 mV for a current density of 135 mA cm$^{-2}$ at 80°C. This is perhaps the lowest value so far reported for an electrode material thus demonstrating that the combination of properties explored here (intrinsic activity and surface area) is a feasible alternative for the development of active electrode materials for water electrolysis.

To assess the stability of the cathodes under continuous operation conditions, long-time electrolyses were carried out in 6 M KOH solutions at 70°C using a constant current density of 135 mA cm$^{-2}$ for 500 h. In addition, the electrolyses were subjected to shutdowns to simulate situations that are common in industrial plants. Thus, a 2 h stop (open circuit condition) was imposed to the system after 180 h while a second one lasting 6 h was performed after 360 h. Fig. 5 shows the cathode overpotential variations for Ni–Fe–Mo
Fig. 2. AFM images for the Ni–Fe–Mo coating as prepared and for type-b* Ni–Fe–Mo–(Zn) after alkaline leaching and corresponding profiles recorded across the samples.
Table 1
Electrode surface (EDX) and plating solution compositions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>Ni (at%)</th>
<th>Fe (at%)</th>
<th>Mo (at%)</th>
<th>Zn (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plating solution 1</td>
<td></td>
<td>71.3</td>
<td>16.7</td>
<td>12.0</td>
<td></td>
</tr>
<tr>
<td>Ni–Fe–Mo deposit</td>
<td></td>
<td>51.4</td>
<td>5.5</td>
<td>43.1</td>
<td></td>
</tr>
<tr>
<td>Plating solution 2</td>
<td></td>
<td>67.8</td>
<td>16.0</td>
<td>11.4</td>
<td>4.8</td>
</tr>
<tr>
<td>Ni–Fe–Mo–Zn (type-a)</td>
<td></td>
<td>51.7</td>
<td>4.7</td>
<td>40.6</td>
<td>3.0</td>
</tr>
<tr>
<td>Ni–Fe–Mo–(Zn) (type-a*)</td>
<td></td>
<td>71.1</td>
<td>12.7</td>
<td>15.1</td>
<td>1.1</td>
</tr>
<tr>
<td>Ni–Fe–Mo–Zn (type-b)</td>
<td></td>
<td>50.3</td>
<td>7.2</td>
<td>34.8</td>
<td>7.7</td>
</tr>
<tr>
<td>Ni–Fe–Mo–(Zn) (type-b*)</td>
<td></td>
<td>70.9</td>
<td>15.3</td>
<td>12.7</td>
<td>1.1</td>
</tr>
</tbody>
</table>

*EDX surface composition after alkaline leaching.

Fig. 3. Steady-state polarisation curves for the HER in 6 M KOH showing a comparison between the different cathodes under investigation and bright Ni at 25°C.

Fig. 4. Steady-state polarisation curves for HER in 6 M KOH at different temperatures for (type-b*) Ni–Fe–Mo–(Zn) coatings after hot alkaline leaching.

and for (type-b*) Ni–Fe–Mo–(Zn) electrodes with time.

As can be observed from Fig. 5, both materials undergo an initial activation that is slowly lost as the electrolyses proceed. The first stop (short duration) has little effect on that tendency while the second and longer one produces an activation that is rapidly obscured by stabilisation of the overpotential at around 157 mV after 440 h. Although the

Table 2
Electrochemical parameters for the HER in 6 M KOH at different temperatures

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Ni–Fe–Mo</th>
<th>type-b* Ni–Fe–Mo–(Zn)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>b (mV dec⁻¹)</td>
<td>η₁₃₅ (mV)</td>
</tr>
<tr>
<td>25</td>
<td>57.6</td>
<td>164</td>
</tr>
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<td>30</td>
<td>57.4</td>
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<td>50</td>
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<td>60</td>
<td>46.6</td>
<td>108</td>
</tr>
<tr>
<td>70</td>
<td>45.8</td>
<td>99.1</td>
</tr>
<tr>
<td>80</td>
<td>41.5</td>
<td>87.5</td>
</tr>
</tbody>
</table>
Fig. 5. Cathode overpotential variations for Ni–Fe–Mo and for (type-b∗) Ni–Fe–Mo–(Zn) with time in 6 M KOH at 70°C under a constant current density of 135 mA cm⁻² for 500 h. The electrolyses were subjected to a shutdown of 2 h (open circuit condition) after 180 h and of 6 h after 360 h.

Fig. 6. SEM analyses of the electrode surfaces after long-time electrolysis.

The performance of these two materials decays with electrolysis time, the final result is still very promising from an industrial viewpoint.

Fig. 6 corresponds to SEM analyses of the electrode surfaces after long-time electrolysis and shows a considerable degradation of the coatings, particularly in the case of Ni–Fe–Mo, that must be due to the removal of Mo species when in contact with the hot alkali, as suggested by EDX analysis, which indicated a diminishing of Mo concentration in the coating from 43.1 to 18.3 at%. Nevertheless, the type-b∗ Ni–Fe–Mo–(Zn) coating remains on the surface in an appreciable quantity and clearly shows a large electrochemical area.

4. Conclusions

The improved co-deposition technique described in this work produces adherent Ni–Fe–Mo–(Zn) coatings after alkaline leaching of the Zn from the surface. The resulting material shows very low overpotential values for the her in concentrated basic solutions at all temperatures and its performance could be further improved by increasing the surface area. The value recorded at 80°C under a current density of 135 mA cm⁻² in 6 M KOH (η = 83.1 mV) is amongst the lowest so far reported in the literature. Although the performance of the coatings decay with time reaching 157 mV after 440 h of constant current electrolysis they still can be considered as promising cathodes for industrial water electrolysis.

Acknowledgements

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References