Electrodeposition mechanism and characterization of Ni–Mo alloy and its electrocatalytic performance for hydrogen evolution

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In the study, the electrodeposition mechanism of Ni–Mo alloy was investigated. Potentiostatic deposition showed that the presence of MoO₄²⁻ could reduce the deposition overpotential of Ni, and the deposition current efficiency of Ni–Mo alloy was lower than pure Ni deposition as the potential moved negatively. Cyclic Voltammetry (CV) indicated that both the first reduction peak for Ni deposition and the deposition peak of Ni–Mo alloy moved to more positive potentials as the content of Ni²⁺ increased, but the deposition peak of Ni–Mo alloy moved to more negative potentials as the content of MoO₄²⁻ increased. The cathodic polarization curve on Rotating Disc Electrode (RDE) presented that Ni–Mo codeposition was controlled by charge transfer. The morphology, composition and structure of Ni–Mo alloy were characterized by SEM, EDS and XRD. The results showed the Ni–Mo alloy coatings exhibited a spherical and cauliflower-like pattern, having a considerably rougher surface, with nano-crystal structure when the elements composition was Ni₈₀.₁₄Mo₁₉.₅₉. The electrochemical activity for hydrogen evolution of Ni–Mo alloy was studied in 30 wt.% KOH at 25 °C using steady-state polarization and electrochemical impedance spectroscopy (EIS) methods. The results clearly demonstrated that an increase in the electrochemical activity for hydrogen evolution of the Ni–Mo alloy coating can be attributed both higher exchange current density and larger real electrode area.

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I n t r o d u c t i o n

Ni–Mo alloys are interesting for their hardness, thermal [1], corrosion resistance, magnetic and catalytic properties [2–6], especially for their ability to catalyze the hydrogen evolution reaction of water electrolysis [7–10]. According to the theory of electrocatalysis, the electrocatalytic activity depends on the heat of adsorption of the intermediate on the electrode surface defined by the well-known “volcano” curve [11]. It is clear that beside the precious metals, there is practically no

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way to find the new materials among pure metals, which would possess high catalytic activity for the hydrogen evolution reaction (HER). So the alloying of two (or more) metals has long appeared as the most straightforward approach to achieve electrocatalytic activity for the HER, such as Ni–Mo, Ni–Zn, Ni–Fe, Ni–W, Ni–Mo–B, Ni–Mo–Fe, Ni–Mo–Zr, Ni–Mo–Cu, Ni–Co–Mo, Ni–Fe–Co–Mo and so on [12–22]. Miles [23] suggested that a combination of two metals from the two branches of the “volcano” curve could result in enhanced activity for the HER. Thus, the Mo-based alloys became the main objective of the research during the past 30 years, and the Ni–Mo alloy showed superior qualities, of which in the bulk form exchange current densities were between $10^{-6}$ and $10^{-4} \text{ A} \cdot \text{cm}^{-2}$, compared to $10^{-3} \text{ A} \cdot \text{cm}^{-2}$ for that of Pt [24].

There are many methods for preparing Ni–Mo alloy applied in catalyzing the hydrogen evolution reaction, such as ball milling, machine alloying, composite electrodeposition, electrodeposition and so on. James [25] reported a method for generating unsupported nanopowders of Ni–Mo, which can be suspended in common solvents and cast onto arbitrary substrates. The mass-specific catalytic activity under alkaline conditions approaches that of the most active reported non-noble HER catalysts, but the coatings degrade after operation for a few hours under acidic conditions. Compare to other methods, electrodeposition has been widely used to obtain more stable, longer service life and higher catalysis activity Ni–Mo alloys. Guettaf [26] investigated that the catalytic activity for the hydrogen evolution of Ni–Mo alloy coatings varied with the Mo content in the Ni–Mo alloy. Genneno [27] thought that Ni–Mo alloy had high catalytic activity for the hydrogen evolution because of the rougher electrode surface and porous structure. However, it is difficult to control Mo content and obtain rougher surface because of the complicated electrodeposition mechanism of Ni–Mo alloy. As a result, it is of much significance to study electrodeposition mechanism of Ni–Mo alloy. Although the electrodeposition of Ni–Mo alloy has been described as induced codeposition by Brenner [28], since molybdenum cannot be deposited alone from an aqueous bath, but only in the presence of Ni$^{2+}$. Some researchers also studied the different mechanisms to explain certain features of the induced codeposition behavior [29], they did not adequately predict the influence of electrolyte composition on resulting alloy deposition. Therefore, a more quantitative approach is needed in order to reach a better understanding of the mechanism of induced codeposition for Ni–Mo alloy.

The deposition process of Ni–Mo coatings on the Pt electrode was studied by Potentiostatic deposition and Cyclic Voltammetric. Ni–Mo alloy coatings were electrodeposited by potentiostatic deposition method at different deposition potentials to obtain cathodic polarization and current efficiency. The cathodic polarization curve on Rotating Disc Electrode (RDE) was used to study the electrode process dynamics. The surface morphology, composition and microstructure of the Ni–Mo alloy coatings were also characterized in detail. The catalytic activity of hydrogen evolution of Ni–Mo alloy was investigated by steady-state polarization curves and electrochemical impedance spectroscopy (EIS) experiments.

**Experimental**

**Materials**

All the reagents were analytical grade except saccharin and 1,4-butynediol which were plating grade. All solutions were prepared with secondary distilled water. Nickel sulfate and other reagents were purchased from Sinopharm Chemical Agent Company. Sodium dodecyl sulfate was supplied by Shanghai Chemical Reagent Company, Chinese Academy of Medical Sciences.

**Electrochemical tests for electrodeposition mechanism of Ni–Mo alloys**

The electrochemical measurements were conducted in a conventional three-electrode glass cell. The platinum sheet (99.99% Pt, 2.0 cm$^2 \times 2$) was used as the working electrode (WE). All potentials were referenced to the Hg/HgO, OH$^-$ electrode. Further, a large surface platinum plate was used as the counter electrode (CE). The working electrode was polished by $7^\text{th}$ fine emery papers, and then cleaned by acetone and secondary distilled water successively. An ATA-1B Rotating Disc Electrode (RDE) was also used in the study. The measurements were carried out using a electrochemical workstation(CHI760B) with a link to a microcomputer. The chemical compositions of the electrolytes studied were shown in Table 1.

The Cyclic Voltammetry (CV) tests were carried out in solution C, D, F, G, H, I and J, with 0.01 V/s scanning speed, the scan potential range from 0 to $\pm 1.5$ V.

The cathodic polarization curves on Rotating Disc Electrode (RDE) were studied in solution C and D, with 0.01 V/s scanning speed, the scan potential range from 0.4 to $\pm 1.5$ V, and the rotating speeds were 500 r·min$^{-1}$, 1000 r·min$^{-1}$, 2000 r·min$^{-1}$ and 3000 r·min$^{-1}$ successfully.

In order to determine the contents of Ni and Mo on the Pt electrode, the depositions were obtained by potentiostatic deposition for 80 min, at 25 °C. The 13 kinds various potential values were selected from $-0.7 \text{ V}$ to $-1.3 \text{ V}$(vs Hg/HgO) with 0.05 V intervals. Then, the contents of Ni and Mo on the Pt electrode were determined by UV–visible spectrophotometric method [30] . And then, the average deposition current density $j$ was calculated by the formula: $j = \frac{\text{q}}{t} \left( \frac{\text{mol}}{\text{s}} \right)$ ($\text{q}$ was the electron number of metal reduction, $m$ was mass of metal, $F$ was Faraday’s constant, $S$ was the area of the working electrode, $t$ was the time for electrodeposition, and the $M$ was the molar mass of metal). And current efficiency $\eta$ can be calculated by the formula: $\eta = \frac{j}{i_m} \left( \frac{\text{mol}}{\text{s}} \right)$ ($i_m$ was current density of metal reduction, $j$ was the total current density). Finally, the polarization curves and current efficiency curves of Pt electrode were drawn according to the average deposition current density $j$ and current efficiency $\eta$ at various potential values.

**Preparation of Ni–Mo alloy electrolytes**

Copper foils (99.9%), 2 cm wide and 3 cm long, were used as cathode substrates to electrodeposit Ni–Mo alloy. Pure Ni plates, twice the size of the cathodes, were used as anode
The composition of solutions considered in present study.

<table>
<thead>
<tr>
<th>Solutions</th>
<th>NiSO₄·6H₂O g·L⁻¹</th>
<th>Na₂MoO₄·2H₂O g·L⁻¹</th>
<th>Na₄(C₂H₇O₂)₂·2H₂O g·L⁻¹</th>
<th>NH₃·H₂O mL</th>
<th>NaCl g·L⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>0</td>
<td>120</td>
<td>100</td>
<td>10</td>
</tr>
<tr>
<td>B</td>
<td>0</td>
<td>30</td>
<td>120</td>
<td>100</td>
<td>10</td>
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<tr>
<td>C</td>
<td>60</td>
<td>0</td>
<td>120</td>
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</table>

substrates. Before the electrodeposition, all non-working surfaces were insulated. The copper foils were polished to a mirror finish with 1, 3, and 5 fine emery papers successively, and then treated with acetone. After that, the copper foils were dipped into 10% HCl solution for 1 min followed by a wash with secondary distilled water. The plating bath compositions of the Ni–Mo alloy electrodeposition were shown as follows: 60 g·L⁻¹ NiSO₄·6H₂O, 20–40 g·L⁻¹ Na₂MoO₄·2H₂O, 120 g·L⁻¹ Na₃Cit·2H₂O, 100 mL/L NH₃·H₂O, 10 g·L⁻¹ NaCl, 1 g·L⁻¹ saccharin, 0.2 g·L⁻¹ 1,4-butynediol, 0.1 g·L⁻¹ sodium dodecyl sulfate, pH at 9. The electrodeposition was carried out at a current density of 12 A·dm⁻² for 30 min. The temperature was maintained at 50 °C.

Characterization

The surface morphologies of the Ni–Mo alloy electrodes with different Mo content were analyzed using JSM-6700F scanning electron microscope (SEM). The elemental compositions of the electrode were examined using a JSM-6700F field emission scanning electron microscope equipped with Oxford Instruments EDS. The structure was characterized by D8 Advance XRD Bruker X-ray powder diffraction (CuKα λ = 1.5418 Å).

Electrochemical characterizations of Ni–Mo alloy electrode for hydrogen evolution in alkaline solution were carried out by steady-state polarization curves and EIS. A three-electrode glass cell similar to that of the electrodeposition mechanism experiments was used, with electrodeposited Ni–Mo alloy as the working electrode instead of the platinum sheet. The electrolyte was alkaline solution with 30 wt.% KOH at 25 °C.

Steady-state polarization curves were performed in the potential range from ~1.50 V up to the equilibrium potential at a scan rate of 1 mV·s⁻¹. Steady-state polarization curves was used to determine the kinetic parameters of the HER. For the linear part of the steady-state polarization curves, the kinetic equation can be written as \( \log j = \log j_0 + \eta/b \) if was the measured current density, \( j_0 \) was the exchange current density, \( \eta \) was the applied overpotential and \( b \) was the Tafel slope.

EIS was an appropriate technique to determine the real surface area and to further investigate the electrochemical activity of the electrode materials for the HER. EIS measurements were performed at \( \eta = 0 \) mV in a frequency range between 10 kHz and 0.01 Hz with an amplitude of 5 mV. The acquired data were curve fitted and analyzed by the complex impedance plane analysis method using EIS 300 software.

Before recording the steady-state polarization curves as well as the EIS measurements, the Ni–Mo alloy electrodes were cathodically polarized at a current density of ~100 mA·cm⁻² for 15 min, causing the evolution of hydrogen gas.

Results and discussion

Cathodic polarization

In order to investigate the electrochemical behaviors of Ni–Mo, the polarization curves of solution without NiSO₄ and Na₂MoO₄, Mo solution containing 30 g·L⁻¹ Na₂MoO₄·2H₂O, Ni solution containing 60 g·L⁻¹ NiSO₄·6H₂O, and Ni–Mo solution containing 60 g·L⁻¹ NiSO₄·6H₂O and 30 g·L⁻¹ Na₂MoO₄·2H₂O on the Pt electrode were carried out, and the results were shown as Fig. 1. On the one hand, according to Fig. 1(a), there was not any metal deposition but hydrogen reduction on the Pt electrode, because of no metal ion in solution A. Fig. 1(b) was similar to Fig. 1(a), there was no Mo deposition on the Pt electrode. It was visible that it was impossible for Mo to reduce alone in alkaline citrate solution. On the other hand, For Fig. 1(c), the reduction current was smaller, and the start

![Fig. 1 – The polarization curves on the Pt electrode in solutions of various composition. (a-solution A, 0 g·L⁻¹ NiSO₄·6H₂O + 0 g·L⁻¹ Na₂MoO₄·2H₂O, b-solution B, 0 g·L⁻¹ NiSO₄·6H₂O + 30 g·L⁻¹ Na₂MoO₄·2H₂O, c-solution C, 60 g·L⁻¹ NiSO₄·6H₂O + 0 g·L⁻¹ Na₂MoO₄·2H₂O, d-solution D, 60 g·L⁻¹ NiSO₄·6H₂O + 30 g·L⁻¹ Na₂MoO₄·2H₂O).](image-url)

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reduction potential was more negative than that in Fig. 1(a) and (b). This was due to the deposition of Ni in the solution C, and the Ni deposition on the surface of Pt electrode reduced the catalytic activity of hydrogen evolution, which made the cathodic polarization increased, and the current decreased. However, as seen from the curve Fig. 1(d), the current was larger and the start reduction potential kept consistent with Fig. 1(a) and (b). This was because the Ni–Mo alloy codeposited on the surface of Pt electrode. The presence of MoO₄²⁻ reduced the Ni deposition potential and Ni can induce MoO₄²⁻ reduction. The Ni–Mo alloy codeposited on the surface of Pt electrode had high catalytic activity for hydrogen evolution, so the cathodic polarization decreased, and the current increased more.

**Kinetics of separate reduction of Ni**

Fig. 2 presented the total polarization curve, the branch polarization curve and the relationship between current efficiency and potential on the Pt electrode in solution C containing 60 g·L⁻¹ NiSO₄·6H₂O without Na₂MoO₄. Fig. 2(b) showed that Ni began to deposit when the potential was about −0.9 V. The Ni deposition became slow when the potential ranged from −0.9 V to −1.0 V, and the cathodic current was mainly used for hydrogen evolution. When the potential was lower than −1.0 V, the deposition current of Ni increased rapidly, and the deposition rate of Ni was much higher than hydrogen evolution. From Fig. 2(d), it can be found that the deposition efficiency increased rapidly when the potential changed between −1.0 V and −1.10 V. Moreover, when the potential reached −1.10 V, the current efficiency kept stable. It indicated that the deposition efficiency of Ni was higher at a low potential in the solution C.

Fig. 3 showed the Cyclic Voltammetry (CV) on Pt electrode in different concentration of Ni²⁺ without MoO₄⁻ solutions. In Fig. 3, there were two reduction peaks for Ni. Because the reduction of Ni²⁺ had two steps [31]: (1) NiCit⁺ + e⁻ → NiCit²⁻_ads; (2) NiCit²⁻_ads + e⁻ → Ni(s) + Cit⁻. More, the potential of the first reduction peak shifted positive with the increase of the concentration of Ni²⁺. This was because the increase of

**Fig. 2** The polarization curves and current efficiency on the Pt electrode in solution C containing 60 g·L⁻¹ NiSO₄·6H₂O without Na₂MoO₄. (a-total polarization curve, b-polarization curve of Ni, c-polarization curve of H₂, d-electrodeposition current efficiency of Ni).

**Fig. 3** The cyclic voltammetry curves on the Pt electrode in different Ni²⁺ concentration solutions. (a-solution C, 60 g·L⁻¹ NiSO₄·6H₂O + 0 g·L⁻¹ Na₂MoO₄·2H₂O, b-solution E, 40 g·L⁻¹ NiSO₄·6H₂O + 0 g·L⁻¹ Na₂MoO₄·2H₂O, c-solution F, 20 g·L⁻¹ NiSO₄·6H₂O + 0 g·L⁻¹ Na₂MoO₄·2H₂O).

**Fig. 4** The cathodic polarization curves on the RDE at different rotating speeds in solution C containing 60 g·L⁻¹ NiSO₄·6H₂O without Na₂MoO₄.

The polarization curves on the Pt electrode in solution D containing 60 g·L⁻¹ NiSO₄·6H₂O and 30 g·L⁻¹ Na₂MoO₄·2H₂O were shown as Fig. 6. For one hand, from Fig. 6(b), Ni began to deposit at −0.85 V, which shifted 0.05 V positive compared

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with the potential of Ni deposition on the Pt electrode in solution C. Because the presence of MoO$_4^{2-}$ made the deposition of Ni easy, and the deposition potential shifted positively. For the other hand, in Fig. 6(d), the current of side reactions increased with the potential shifting negative at the beginning. Because except hydrogen evolution, the [NiCitMoO$_2$]$_{ads}$ and other intermediate products produced. However, the current of side reactions began to decrease when the potential reached -1.25 V. The reason was that the generation of [NiCitMoO$_2$]$_{ads}$ was blocked by a large number of metal deposition and amassing of [NiCitMoO$_2$]$_{ads}$ intermediate products. Moreover, the [NiCitMoO$_2$]$_{ads}$ occupied a large number of reactive sites on the cathode which inhibited hydrogen evolution and reduced the current of side reaction.

Fig. 7 presented the cathodic polarization curve in solution D containing 60 g·L$^{-1}$ NiSO$_4$·6H$_2$O and 30 g·L$^{-1}$ Na$_2$MoO$_4$·2H$_2$O on the RDE at different rotating speeds. and the reduction potential of MoO$_4^{2-}$ too close and difficult to distinct. On the other hand, the peak current didn’t change with the increasing of the rotating speed. It reflected that the rate determining step in Ni–Mo codeposition was charge transfer.

The effect of concentration of MoO$_4^{2-}$ on the deposition of Ni–Mo alloy keeping NiSO$_4$·6H$_2$O concentration at 60 g·L$^{-1}$ constant was shown in Fig. 8. As we can see that there was only one reduction peak. And the potential of reduction peak shifted negative with increasing the concentration of MoO$_4^{2-}$. This reflected the concentration of MoO$_4^{2-}$ affected the deposition potential of Ni–Mo alloy. Fig. 9 showed the effect of concentration of Ni$^{2+}$ on the deposition of Ni–Mo alloy keeping Na$_2$MoO$_4$·2H$_2$O concentration at 30 g·L$^{-1}$ constant. The potential of reduction peak shifted positive with increasing the concentration of Ni$^{2+}$. It was consistent with the behavior of Pt electrode in solution C.

The relationship between current efficiency and potential of solution C and D on the Pt electrode was shown as Fig. 10. Compared Fig. 10(a) with Fig. 10(c), the deposition current efficiency of Ni in solution D was greater than the deposition
Fig. 9 — The cyclic voltammetry curves on the Pt electrode in different Ni^{2+} concentration solutions. (a—solution D, 60 g·L^{-1} NiSO_{4}·6H_{2}O + 30 g·L^{-1} Na_{2}MoO_{4}·2H_{2}O, b—solution I, 40 g·L^{-1} NiSO_{4}·6H_{2}O + 30 g·L^{-1} Na_{2}MoO_{4}·2H_{2}O, c—solution J, 20 g·L^{-1} NiSO_{4}·6H_{2}O + 30 g·L^{-1} Na_{2}MoO_{4}·2H_{2}O).

Fig. 10 — The relationship between current efficiency and potential in solution C containing 60 g·L^{-1} NiSO_{4}·6H_{2}O and D containing 60 g·L^{-1} NiSO_{4}·6H_{2}O and 30 g·L^{-1} Na_{2}MoO_{4}·2H_{2}O on the Pt electrode (a—Ni of solution C, b—Ni–Mo of solution D, c—Ni of solution D).

Fig. 11 — The relationship between Ni deposition current and potential of solution C containing 60 g·L^{-1} NiSO_{4}·6H_{2}O and D containing 60 g·L^{-1} NiSO_{4}·6H_{2}O and 30 g·L^{-1} Na_{2}MoO_{4}·2H_{2}O on the Pt electrode.

relative with the deposition mechanism of Mo^{6+}: (3) \( \text{MoO}_{4}^{2-} + 2\text{H}_{2}\text{O} + 2\text{e}^- \rightarrow \text{MoO}_{3} + 4\text{OH}^- \); (4) \( \text{NiCit}^- + \text{MoO}_2\rightarrow [\text{NiCitMoO}_2]_{ads} \); (5) \( [\text{NiCitMoO}_3]_{ads} + 2\text{H}_{2}\text{O} + 4\text{e}^- \rightarrow \text{Mo} + \text{NiCit}^- + 4\text{OH}^- \). Because the \( [\text{NiCitMoO}_3]_{ads} \) occupied a portion of activity center on the substrate, together with the reduction of Ni^{2+} was inhibited, the total current efficiency reduced.

**Morphologies**

In order to examine the surface microstructure of the electroactive coatings used in research, a scanning electron microscopy (SEM) technique was used. Energy dispersive spectrometry (EDS) was further used in order to determine the chemical composition of the coatings. Fig. 12 showed the SEM micrographs of the Ni–Mo alloy coatings with different Mo content. On the one hand, the crystal growth of Ni–Mo alloy was three-dimensional growth model. On the other hand, Mo content in Ni–Mo alloy effected the morphologies of the Ni–Mo alloy coating. From Fig. 12(a), the surface morphology of the Ni–Mo alloy coating was composed of different sizes of spherical, when the Mo content of the Ni–Mo alloy coatings was 11.47 at.%. In the Fig. 12(b), while the Mo content of the Ni–Mo alloy coatings was 19.59 at.%, it can also be seen that the Ni–Mo alloy coatings exhibited a spherical(globular) and cauliflower-like pattern, having a considerably rougher surface. It can also be observed that some smaller ellipsoid-shaped globules appear on top of the larger globules. The borders of both smaller and bigger globules were circular or quasi-circular. However, the Ni–Mo alloy coatings didn’t exhibit spherical but irregular and small granular salient, and the coatings was relative black and loose, the quality of the coatings decreased, when the Mo content of the Ni–Mo alloy coatings was 25.25 at.%. (a) Ni–Mo alloy codeposition increased slowly and was lower than the deposition efficiency of Ni in solution C as the potential shifting negative. It was possibly

XRD

X-ray diffraction (XRD) was used for the structural characterization of the Ni–Mo alloy coating. In Fig. 13, as we have...
seen, there was a typical diffraction peak at 2θ angles of about 45° corresponding to the reflections of (111) crystalline planes of the face-centered cubic structure of the Ni-Mo [32]. Analyzing the result calculated according to Scherrer formula, the Ni–Mo alloy coating was nano-crystal structure. This structure can effectively reduce the adsorption activation energy of hydrogen on the alloy electrode surface, and the catalytic activity for hydrogen evolution of Ni–Mo alloy was improved.

Electrocatalytic activity of the electrode

Steady-state polarization

In order to investigate the electrocatalytic activity of the prepared catalytic coatings, steady-state polarization measurements were made, and the corresponding electrochemical parameters were derived from the recorded curves. The steady-state polarization curves obtained for HER in the 30 wt.% KOH solution on the Ni and Ni–Mo coatings (Mo 19.59 at.%) were showed in Fig. 14. The Ni–Mo alloy electrode had a much better catalytic activity than the pure Ni electrode. On the one hand, The hydrogen evolution overpotential of Ni–Mo alloy was 152 mV when the current density was 100 mA cm⁻² (η₁₀₀ = 152 mV). It was 293 mV lower than pure Ni. On the other hand, the exchange current density of Ni–Mo alloy was 832.3 times that of pure Ni. The exchange current density was closely related to catalytic activity for hydrogen evolution. The bigger exchange current density, the higher catalytic activity for hydrogen evolution.

EIS

According to Fig. 15(a), which showed the Nyquist diagrams of the Ni and Ni–Mo coatings (Mo 19.59 at.%) electrode in the 30 wt.% KOH solution at 25 °C at ηHER = 0 mV. The double layer can be represented by the electrical equivalent circuit diagrams to model the metal/solution interface. The electrical equivalent circuit diagram was given in Fig. 15(b), this model was applied in the electrode system ignored concentration polarization, which consists of the solution resistance (R_s), in series with a C_d–Rct elements [33]. The charge-transfer resistance (Rct) and the double layer capacitance (C_d) presented in Table 2. The C_d was calculated using equation [34]:

\[ \frac{1}{ω C_d} = \frac{1}{ω C_d} \]

where \( ω \) was the frequency corresponding to the vertex of semicircle. As we can see, the charge-transfer resistance (Rct) of Ni–Mo coatings was much smaller than its of pure Ni, it indicated that the hydrogen evolution reaction took more easily on the Ni–Mo alloy than pure Ni. More, the roughness of Ni–Mo alloy was more than 60 times that of pure Ni, the larger roughness for Ni–Mo alloy, the higher catalytic activity for hydrogen evolution.

Sum up, the Ni–Mo alloy had good electrocatalytic activity for hydrogen evolution because of higher exchange current

Fig. 12 – SEM micrographs of different Mo content of the Ni–Mo alloy coatings. (a) 11.47 at.%; (b) 19.59 at.%; (c) 25.25 at.%. 

Fig. 13 – X-ray diffraction patterns of Ni–Mo alloy coating.

Fig. 14 – The steady-state polarization curves obtained for HER in the 30 wt.% KOH solution at 25 °C on Ni and Ni–Mo coatings.
density and larger real electrode area, which were energy and geometric factor.

Conclusions

In this study, the electrodeposition behavior of Ni–Mo alloy have been investigated. Potentiostatic deposition showed that the presence of MoO$_4^{2-}$ could reduce the deposition over-potential of Ni, and the deposition current efficiency of Ni–Mo alloy was lower than pure Ni as the potential moved negatively. Cyclic Voltammetry indicated that both the first reduction peak for Ni deposition and the deposition peak of Ni–Mo alloy moved to more positive potentials as the content of Ni$^{2+}$ increased, but the deposition peak of Ni–Mo alloy moved to more negative potentials as the content of MoO$_4^{2-}$ increased. The cathodic polarization curve on RDE presented that Ni–Mo codeposition was charge transfer, and pure Ni was charge transfer and diffusion.

The Ni–Mo alloy coatings with various chemical compositions were electrochemically deposited on a copper and characterized by different techniques in view of their possible applications as electrocatalytic materials for the HER in alkaline medium. The Ni–Mo alloy coatings exhibited a spherical and cauliflower-like pattern, having a considerably rougher surface with nano-crystal structure when the Mo content of the Ni–Mo alloy coatings was 19.59 at.%, and the Mo content in Ni–Mo alloy affected the morphologies of the Ni–Mo alloy coating. According to steady-state polarization and EIS test results, an increase in the electrochemical activity for hydrogen evolution of the Ni–Mo alloy coating can be attributed both higher exchange current density and larger real electrode area.

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R E F E R E N C E S