Preparation of nanostructured Co–Mo alloy electrodes and investigation of their electrocatalytic activity for hydrazine oxidation in alkaline medium

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Cobalt and cobalt–molybdenum alloy electrodes are prepared by galvanic deposition on copper substrates. In this paper, we report a study on the influence of alloying cobalt with molybdenum for the oxidation of hydrazine in 1 M NaOH aqueous solutions. The electrocatalytic properties of the electrodes are studied by cyclic voltammetry (CV), chronoamperometry (CA), and electrochemical impedance spectroscopy (EIS). Scanning electron microscopy (SEM), X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS) and inductively coupled plasma (ICP) analysis demonstrate that the structural features and compositions of the as-prepared Co–Mo coatings vary with the deposition conditions. Electrochemical characterization indicates that the electrochemical properties and the electrocatalytic activity of the investigated alloys were strongly dependent on the microstructural features obtained under different deposition conditions. The overall experimental data indicate that alloying cobalt with molybdenum metal leads to an increase of the electrocatalytic activity in hydrazine electrooxidation compared to when using the pure cobalt electrode. High catalytic efficiencies were achieved on Co/25 at.% Mo and Co/33 at.% Mo electrodes, the latter being the best electrocatalyst for hydrazine electrooxidation.

KEYWORDS
cyclic voltammetry, electrocatalytic activity, electrochemical impedance spectroscopy, electrodeposition, hydrazine electrooxidation, nanostructured Co–Mo

1 | INTRODUCTION

Today, fuel cells, operating on methanol or ethanol oxidation as the fuel at the anode and the reduction of oxygen at the cathode, are considered attractive power sources because of their characteristics such as high conversion efficiency/ high power density, low pollution, and light weight. However, the efficiency and power output of direct alcohol fuel cells (DAFCs) are rather low because of the severe susceptibility to poisoning of the anode catalyst due to reaction intermediates such as CO and methanol crossover through the polymer electrolyte membrane. Although hydrazine (N₂H₄) can be absorbed through the skin, affecting the human hematologic system, and is recognized in pharmacology as an established carcinogenic and hepatotoxic chemical leading to severe liver and kidney damages, it is an ideal fuel for a direct fuel cell system because it does not emit environmentally unfriendly materials such as CO₂. Also, the thermodynamic reversible potential of the direct hydrazine fuel cell (DHFC) is quite high, being about 1.56 V. Furthermore, previous studies have revealed that no catalyst poisoning occurs during hydrazine oxidation.
electrooxidation. The use of an alkaline solution in a fuel cell has numerous advantages, including increased efficiency, higher efficiency of both anodic and cathodic processes, availability of a much broader range of possible electrode materials with almost no sensitivity to the surface structure, and insignificant poisoning effects. The hydrazine fuel cell was investigated intensively in the 1960s and 1970s as an alkaline fuel cell (AFC) using a liquid alkaline electrolyte. The electrochemical oxidation of hydrazine in alkaline media can take place through a four-electron process described by the following equation:

$$\text{N}_2\text{H}_4 + 4\text{OH}^- \rightarrow \text{N}_2 + 4\text{H}_2\text{O} + 4e^-$$

Concerted research work has been carried out to search for active electrocatalysts for hydrazine oxidation mainly with the aim of developing high-performance hydrazine fuel cells. Pt-based alloys have been considered the most active electrocatalyst for this reaction. However, the cost and limited supply of Pt constitute major barriers to the development of DHFCS. It is therefore of interest to investigate low-cost and non-noble metals and their alloys, as well as their oxides, for the electrocatalysis of the hydrazine oxidation reaction (HOR) in an alkaline medium.

To date, very few studies have been made on the electrocatalytic properties of Co–Mo alloys for hydrazine oxidation. In this study, for the first time, we investigate the electrocatalytic properties of Co–Mo alloys prepared from a tartrate bath for the oxidation of hydrazine and compare them with those of a pure cobalt electrode.

2 | EXPERIMENTAL

The electroactive coating on Cu substrates was done by electrodeposition via a galvanostatic system. The bath composition and deposition conditions are listed in Table 1. After the deposition of the active electrocatalyst material, the electrode surface was carefully rinsed with a large amount of triply distilled water in order to remove any residues of bath chemicals and unattached catalyst particles.

The phase composition and structure of the pure Co and Co–Mo coatings were determined by X-ray diffraction (XRD) using an X-ray diffractometer model APD 2000 (G.N.R. srl, Novara, Italy) with a Cu Kα radiation source (wavelength = 0.15406 nm).

The morphology and composition of the nanocomposite coatings were characterized with a field-emission scanning electron microscope (TESCAN MIRA3; Pleasanton, CA, USA); the energy-dispersive X-ray (EDX) experiments were also carried out on the same SEM apparatus. Chemical analysis of the electrodedeposited alloys was carried out by means of inductively coupled plasma (ICP) analysis (VARIAN/Vista-PRO, USA).

The electrocatalytic activity of Co and Co–Mo coatings for the oxidation of hydrazine was studied in 1 M NaOH solution. The electrolytes were made up of analytical grade chemicals dissolved in triply distilled water. Aqueous mixtures of N,N-diyethylethanolamine (DEEA) and piperazine (PZ) were used for CO2 removal from the alkaline solution because of the high CO2 loading capacity of DEEA and the high reactivity of PZ. A standard three-electrode cell arrangement was used in all experiments. A platinum sheet of geometric area of ~20 cm2 was used as counter-electrode, while all potentials were measured with respect to a commercial saturated calomel electrode (SCE). The working electrodes were Co and Co with different percentages of electrocatalytic Mo coatings electrodeposited on a Cu substrate of geometric area 1 cm2.

The electrochemical techniques employed were cyclic voltammetry (CV), chronoamperometry (CA), and electrochemical impedance spectroscopy (EIS). Electrochemical experiments were carried out using a vertex potentiostat/galvanostat (Ivium Technology, The Netherlands) electrochemical analyzer run by the IviumSoft software. The CV and CA experiments were performed in 1 M NaOH + 0.1 M N2H4 solution at 25°C in the potential region from −0.85 to 0.6 V vs. SCE and at a constant potential of 0.2 V vs. SCE, respectively.

The rms amplitude of the sinusoidal potential for the EIS measurements was 10 mV, and the frequency range was 100 kHz–0.01 Hz. The EIS data were curve-fitted and analyzed using the ZView(II) software.

3 | RESULTS AND DISCUSSION

3.1 Composition and morphology of the electrodes

ICP was used to determine the exact composition of the electrocatalytic coatings. The compositions of the different catalysts are presented in Table 2 (in at.%). In order to investigate the influence of the catalyst composition for the electrooxidation of hydrazine, three different alloy compositions were made by changing the electroplating bath composition (Table 1).

The XRD patterns of pure Co and Co–Mo catalysts are shown in Figure 1. Based on the XRD analysis, the presence of Co and Co3Mo phases is clearly seen. The mean
sizes of the crystallites were estimated to be in the range 10.37–21.42 nm, which suggests the formation of nanocrystalline deposits. Some peaks characteristic of copper reflection from substrate are also evident. When the amount of Mo exceeded 25 at.%, only a single broad reflection centered at θ = 41.8° was observed in the diffraction pattern, suggesting that the deposit was completely amorphous. The same results have also been obtained during the electrodeposition of Co–Mo alloy coatings from aqueous electrolytes.[30–34]

In order to examine the morphology of the electroactive coatings used in our study, SEM was used. The SEM images in Figure 2 show significant differences in the morphology of the investigated catalytic coatings. Pure Co (Figure 2a) shows a relatively homogeneous surface of small roughness, which can be considered as a quasi-two-dimensional surface. On the other hand, from Figure 2b–d it can be seen that the Co–Mo coatings show a spherical (globular) shape with a considerably rougher surface than that of the pure cobalt coating. It can also be seen on the micrographs that some smaller ellipsoid-shaped globules appear on top of the larger globules. From Figure 2c it can be seen that the size of the globules is smaller in the CoMo-2 sample, which contains 67at.% Co. The borders of both smaller and bigger globules are circular or quasi-circular, which is quite different from the polygonal form of polycrystals observed on Co, indicating the absence of grain boundaries and the nanocrystalline structure of amorphous CoMo-2 coating. Figure 2d shows the SEM micrograph of the surface morphology of CoMo-3 coating electrodeposited from the highest molybdenum concentration. This deposit showed cracks. In general, solutions with low molybdate concentration (<40 g L⁻¹) gave fine-grained and crack-free deposits with a percentage of molybdenum of <40%.

The EDX spectra obtained from the surfaces of different deposits are given in Figure 3. The analysis of the alloy deposits revealed that they were composed of Co + Mo with a percentage of molybdenum that was a function of the

![TABLE 2](image)

<table>
<thead>
<tr>
<th>Notation of electrode</th>
<th>Formula</th>
<th>At.% Co</th>
<th>At.% Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>Co</td>
<td>100</td>
<td>–</td>
</tr>
<tr>
<td>CoMo-1</td>
<td>Co₃Mo</td>
<td>75</td>
<td>25</td>
</tr>
<tr>
<td>CoMo-2</td>
<td>Co₂Mo</td>
<td>67</td>
<td>33</td>
</tr>
<tr>
<td>CoMo-3</td>
<td>Co₁₂Mo</td>
<td>60</td>
<td>40</td>
</tr>
</tbody>
</table>

![FIGURE 1](image)

**FIGURE 1** X-ray diffraction pattern of as-deposited (a) Co, (b) CoMo-1, (c) CoMo-2, and (d) CoMo-3 from the bath of Table 1

![FIGURE 2](image)

**FIGURE 2** Morphology of the electrode surface after electrodeposition of (a) Co, (b) CoMo-1, (c) CoMo-2, and (d) CoMo-3 from the bath of Table 1

![FIGURE 3](image)

**FIGURE 3** EDX spectra obtained from the surfaces of (a) pure cobalt, (b) Co/25 at.%Mo, (c) Co/33 at.%Mo, and (d) Co/40 at.%Mo coating
solution composition. In other words, the percentage of molybdenum in the deposits could be increased by increasing the molybdate concentration in the solution. The results on the composition obtained using EDX measurements were in reasonable agreement with the ICP measurements.

Figure 4 shows the evolution of the surface morphology of the CoMo-2 alloy coating electrodeposited at temperatures of 30–75°C. According to these images, the CoMo-2 alloys deposited at 30, 45, and 60°C are quite compact with an ordered morphology and composed of very fine grained particles. As the electrolyte temperature was increased to 75°C, the grain boundaries became more pronounced (Figure 4d).

The chemical composition of the CoMo-2 alloy electrodeposited under different temperatures was determined by EDX (Figure 5). All EDX spectra showed the characteristic peaks for Co and Mo. As shown in Figure 5, on increasing the bath temperature from 30 to 75°C, the molybdenum content in the CoMo-2 alloy increased slightly from 27.84 to 36.68 at.%. An interesting fact is that the increase in the electroplating temperature caused an increase in the grain size of the deposits due to the increase of the molybdenum content of the alloy, as shown in Figure 5.

### 3.2 Cyclic voltammetry

In order to compare Co–Mo electrodes with the pure cobalt electrode, cyclic voltammetry was performed. Figure 6 shows cyclic voltammograms of pure Co, CoMo-1, CoMo-2, and CoMo-3 electrodes in 1 M NaOH with and without 0.1M N2H4, at a scan rate of 100 mV s−1. In the case of the alkaline electrolyte, the active ionic species is OH−, and the electrochemical M(II) → M(III) oxide transformation process and electrochemical oxidation of N2H4 at Co electrodes can be represented by

\[
\text{Co} + 2\text{OH}^- \rightarrow \text{Co(OH)}_2 + 2e^- \tag{2}
\]

\[
\text{Co(OH)}_2 + \text{OH}^- \rightarrow \text{CoOOH} + \text{H}_2\text{O} + e^- \tag{3}
\]

\[
4\text{CoOOH} + \text{N}_2\text{H}_4 \rightarrow 4\text{Co(OH)}_2 + \text{N}_2 \tag{4}
\]
Peak (I) can be attributed to the interconversion of Co(OH)$_2$ and CoOOH in alkaline media.$^{[34-36]}$ An increase in the anodic peak current for peak (I) followed by the appearance of a new peak (II) at a more positive potential are the main effects observed upon the addition 0.1 M hydrazine to the electrolyte.

The appearance of this new anodic peak (II) can lead to the conclusion that hydrazine oxidation takes place after the complete oxidation of Co(OH)$_2$ to CoOOH.$^{[34-36]}$ In other words, there is a separation of the Co(OH)$_2$ and CoOOH oxidation peaks due to hydrazine oxidation.

The electrocatalytic oxidation of hydrazine occurs not only during the anodic half-cycle but also in the initial stage of the cathodic half-cycle. Hydrazine molecules adsorbed on the surface are oxidized at higher potentials in parallel with the oxidation of Co(II) to Co(III) species. The latter process has the consequence of decreasing the number of sites for hydrazine adsorption, which tends to decrease the overall rate of hydrazine oxidation. Thus, the anodic current passes through a maximum as the potential is anodically swept. In the reverse half-cycle, the oxidation continues and the corresponding current goes through a maximum as a result of the regeneration of active sites for adsorption of hydrazine due to the removal of adsorbed intermediates and products. The current density for hydrazine oxidation on CoMo-2 electrode (Figure 6c) is greater than that observed for the other electrodes. Two effects were found to be responsible for the observed behavior: an increase in surface roughness, and intrinsic activity of the material. As the content of Mo increases, the electrocatalytic properties of the alloy coating increased, so CoMo-2 electrode was found to yield the highest intrinsic electrocatalytic activity, which can be explained on the basis of the modification of electron density in the d orbitals upon alloying cobalt with molybdenum.

### 3.3 EIS test

In order to electrochemically characterize the real surface of the Co–Mo electrodes with respect to the pure Co electrode, the surface area of the electrodes was determined by recording the impedance plots at the hydrazine electrode oxidation reaction potentials. The Nyquist plots and the equivalent electrical circuit of the impedance of the pure Co and Co–Mo alloy electrodes in 1 M NaOH + 0.1 M hydrazine aqueous solutions at the potential of 0.4 V vs. SCE are shown in Figure 7.

![Experimental Nyquist diagrams and equivalent electrical circuit for hydrazine electrooxidation at pure Co and Co–Mo alloy electrodes in 1 M NaOH + 0.1 M hydrazine aqueous solutions at the potential of 0.4 V vs. SCE](image)

CPE is defined by two parameters, $T$ and $\Phi$, in the equation for the impedance:$^{[39]}

$$Z_{CPE} = \frac{1}{T(j\omega)^{\Phi}}$$

where $Z_{CPE}$ is the CPE impedance, $T$ is the admittance factor, and $\Phi$ is the phase shift, which can be explained as the degree of surface homogeneity.

As can be clearly seen from Figure 7, a so-called pseudo-inductive behavior begins to emerge in the impedance plots, where a large positive loop at higher frequencies is accompanied by a small loop in the fourth quadrant at low frequency, with the diameters of both loops decreasing rapidly with the increase of Mo particles in the coating, as shown in Figure 7. Taking that the average double-layer capacitance ($C_{dl}$) of a smooth metal surface is 20 \( \mu F \) cm$^{-2}$,$^{[40,41]}$ the real surface area of the electrodes can be calculated as $A_{real} = C_{dl}/20$ (cm$^2$), and then the roughness factor, which characterizes the real-to-geometrical surface area ratio, can be calculated from $R_t = A_{real}/A_{geometric}$. For the pure Co and Co–Mo alloy electrodes, the capacitance parameter $T_{dl}$ is related to the average double-layer capacitance $C_{dl}$ by the relation$^{[38]}

$$C_{dl} = \left\{T_{dl}/[R_s^{-1} + R_{ct}^{-1}]^{1-\Phi}\right\}^{1/\Phi}$$

Table 3 shows the mean values of the charge-transfer resistance, double-layer capacitance, true surface, and roughness factor ($R_s$) for the investigated electrodes obtained by fitting the experimental results. In Table 3, the charge-transfer resistance ($R_{ct}$) and CPE-\(\Phi\) values of Co–Mo alloy...
electrodes are lower than those of the pure Co electrode, indicating the rough nature of these deposits. The lowest $R_{ct}$ of 5.301 $\Omega$ cm$^2$ was observed on the nanostructured CoMo-2 electrode. This means that the Co/33 at.%Mo coating shows the highest activity toward hydrazine oxidation of all the investigated coatings. These observations are consistent with the results of CV.

According to the cyclic voltammograms depicted in Figure 6, the CoMo-2 electrode produced about 2 times higher anodic current density compared to that on pure Co electrode in 1 M NaOH + 0.1 M N$_2$H$_4$. However, the real surface area ratio of the CoMo-2 electrode to the Co electrode calculated based on EIS results is about 1.05. Therefore, it can be concluded that, in addition to the increase in the surface area, a major part of the enhanced activity of the CoMo-2 catalyst toward hydrazine electrooxidation is due to the electrocatalytic activity resulting from improvement in the electronic properties of the catalyst. In general, it has been established that low values of $R_{ct}$ and high values of CPE-T imply better electrocatalytic activity of the catalysts.[42–45]

In Table 3, the mean error of the modulus is <5%, indicating a good fitting of the experimental data on the developed equivalent circuit.

### 4 | CHRONOAMPEROMETRY TEST

The catalytic activity and stability of the Co–Mo and pure cobalt electrodes for hydrazine oxidation were investigated by the CA test. Figure 8 shows the CA response of 0.1 M N$_2$H$_4$ on pure Co, CoMo-1, CoMo-2, and CoMo-3 electrodes at a constant potential of 0.2 V vs. SCE. As shown in the figure, the initial current density of the Co–Mo electrodes is significantly higher than that of the pure cobalt electrode. The current decayed more slowly for the Co–Mo electrodes than the pure cobalt electrode, indicating less accumulation of the adsorbed species. The current densities decreased and then stabilized over the experimental period. At the end of the experimental period, the current densities of the Co–Mo electrodes were higher than that of the pure cobalt electrode. This result supports our conclusion about the catalytic role of CoOOH for hydrazine oxidation and that hydrazine oxidation starts directly after the formation of an initial amount of CoOOH on the electrode surface. Also, this implies that the CoMo-2 electrode exhibits the best catalytic activity and stability among these electrodes in an alkaline medium.

### 5 | CONCLUSIONS

In this work, we prepared Co–Mo alloy coatings by electrodeposition from a tartrate bath. Based on XRD investigations, we found that the electrodeposited Co and Co–Mo alloy coatings had nanocrystalline/amorphous structures, with average sizes of the crystallites in the range 10.37–21.42 nm. SEM analyses revealed that the surface morphology of deposits consisted of very small, densely packed crystallites and that the CoMo-2 alloy coating had the highest surface roughness among the investigated coatings. Results of CV, CA, and EIS clearly
demonstrated that alloying Co with Mo resulted in increased electrocatalytic activity in the HOR when compared to pure Co. In CV studies, the Co/33 at.% Mo electrode (CoMo-2) shows a significantly higher response for hydrazine oxidation than pure cobalt and other Co–Mo electrodes. Further, under the CA regime was found that CoMo-2 electrode showed very good resistance against electrode poisoning by hydrazine oxidation intermediates/products. The EIS responses showed that the presence of Mo particles in Co–Mo coatings caused the diameter of the arc to decrease rapidly, indicating that the charge-transfer resistance for the N$_2$H$_4$ electroxidation became smaller. Also, the results of EIS measurement were consistent with those of CV and CA.

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Graphical abstract

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EIS responses show that the presence of Mo particles Co–Mo coatings causes the charge-transfer resistance for hydrazine electroxidation to become smaller. Among these electrodes, the CoMo-2 electrode has the best electrocatalytic activity for hydrazine electroxidation in an alkaline medium. The high activity of CoMo-2 electrode can contribute to the improvement of the electronic properties of the catalyst.