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*V.S. Protsenko, L.S. Bobrova, O.D. Sukhatskyi, F.I. Danilov***ELECTROCATALYTIC BEHAVIOR OF Ni–Mo ALLOY ELECTRODEPOSITED FROM DEEP EUTECTIC SOLVENTS-ASSISTED PLATING BATHS: ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY STUDY****Ukrainian State University of Chemical Technology, Dnipro, Ukraine**

The electrocatalytic behavior of electrodeposited Ni and Ni–Mo alloy coatings in the hydrogen evolution reaction in a 1 M NaOH aqueous solution was investigated by means of the electrochemical impedance spectroscopy method. The electrochemical deposition of electrocatalytic coatings was carried out using electrolytes based on deep eutectic solvents (eutectic mixtures of choline chloride with ethylene glycol or urea). To simulate the recorded Nyquist plots reflecting the electrocatalytic performance of deposited coatings, a modified Armstrong-Henderson equivalent circuit was employed, which accounts for the involvement of adsorbed intermediates in the reaction. The equivalent circuit included three polarization resistances and three constant phase elements, allowing for the consideration of the localization of the electrochemical process on different surface microdomains. It was found that the electrocatalytic activity of nickel coatings deposited from deep eutectic solvents exceeded the activity of nickel fabricated in an aqueous electrolyte. The increase in molybdenum content in the coating was shown to enhance electrocatalytic activity. It was established that the main reasons for improving the electrocatalytic properties of the Ni–Mo alloy coatings are structural-morphological factors (increase in the degree of microheterogeneity of the surface and the development of the surface area available for electrochemical reaction) and the formation of a favorable electronic structure of the metal, leading to the acceleration of the rate-determining Volmer step.

Keywords: deep eutectic solvents, electrodeposition, nickel-molybdenum alloy, hydrogen evolution reaction, electrocatalysis, electrochemical impedance spectroscopy.

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Introduction

The development of advanced electrocatalysts for «green» hydrogen energy is one of the most crucial challenges in contemporary electrochemical science [1,2]. Progress in this direction is closely tied to the design of new electrocatalytic materials that should be relatively inexpensive and accessible, enabling the cathodic hydrogen evolution reaction with minimal polarization. Among various promising alternatives for creating electrocatalysts for electrolytic hydrogen synthesis, considerable attention is focused on nickel-based materials and its alloys [3,4], with one of the

most convenient and accessible methods of production being electrochemical deposition [5,6]. Electrodeposition is traditionally performed from aqueous electrolytes [5], which, despite their apparent advantages, also have some drawbacks. In recent years, researchers have paid significant attention to the electrodeposition of nickel-containing electrocatalysts for hydrogen synthesis from solutions based on a new type of ionic liquids, deep eutectic solvents (DESs) [7]. Electrochemical systems based on DESs differ favorably from those based on water or organic liquids as solvents, as well as from «conventional» low-

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Electrocatalytic behavior of Ni–Mo alloy electrodeposited from deep eutectic solvents-assisted plating baths: electrochemical impedance spectroscopy study

temperature ionic liquids, exhibiting following specific physicochemical and operational advantages: a wide electrochemical stability range allowing for the deposition (co-deposition) of highly electronegative metals; high solubility of various salts and metal oxides; very low saturated vapor pressure; non-volatility; non-flammability; low toxicity; biodegradability; tunability of composition and properties (viscosity, electrical conductivity, etc.) through rational selection of the nature and concentration of components, and other benefits [8].

In our opinion, one of the most promising and successful approaches is the electrodeposition of electrocatalytic nickel-molybdenum coatings from DES-based electrolytes. It is well-known that Ni-Mo alloys exhibit one of the highest electrocatalytic activities towards the hydrogen evolution reaction, comparable to the electrocatalytic properties of platinum [2,3,9]. Recently, we demonstrated the possibility of electrochemical deposition of nickel-molybdenum alloys from plating baths based on deep eutectic solvents [10]. The enhanced electrocatalytic activity of these coatings was confirmed by recording cathodic voltammetric curves and subsequent processing in the Tafel equation coordinates. Although this methodology allows obtaining explicit information about the electrocatalytic behavior of the investigated electrode materials, it still does not provide detailed insights into the mechanism of the electrode process, which is crucial for further improvement of electrocatalytic materials. Therefore, in this study, we employed the electrochemical impedance spectroscopy method to uncover the mechanism of the hydrogen evolution process in an alkaline environment on nickel-based alloys containing molybdenum, the electrodeposition of which was described earlier in the work [10].

Experimental

For the deposition of electrocatalytic coatings, two types of electrolytes were employed based on the so-called ethaline and reline. Ethaline and reline are

established names for two widely used representatives of DESs [8]. Ethaline is a eutectic mixture of choline chloride and ethylene glycol (with the molar ratio of 1:2, respectively), while reline is a eutectic mixture of choline chloride and urea (with the molar ratio of 1:2, respectively). These solvents were supplemented with specific amounts of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ salts, serving as a source of nickel and molybdenum in the electrolytes, respectively. To stabilize the chemical composition of the nickel complexes, all DES-based electrolytes additionally contained 0.5 mol/dm^3 citric acid $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$. The composition of the utilized electrolytes is shown in Table 1. Nickel-molybdenum alloy coatings were deposited at a temperature of 323 K and cathodic current densities of 10, 20, and 30 mA/cm^2 . Nickel coatings (without molybdenum) were deposited at the same temperature and a current density of 10 mA/cm^2 (at higher current densities, it was not possible to obtain coatings well-adhered to the copper substrate). For comparison, coatings were also deposited and investigated from a sulfate-chloride aqueous electrolyte of the Watts type (Table 1) at a temperature of 323 K and a cathodic current density of 10 mA/cm^2 . The thickness of the coatings deposited on the copper substrate was approximately 10 μm . A more detailed methodology for preparing electrolytes and electrochemical deposition of coatings is described in our previous work [10].

The electrocatalytic characteristics of the deposited coatings in the hydrogen evolution reaction at a temperature of 298 K in a 1 M NaOH aqueous alkaline solution, deaerated by purging with purified H_2 , were evaluated in this study using electrochemical impedance spectroscopy. For this purpose, a Reference 3000 potentiostat (USA) with corresponding licensed software was employed. Impedance spectra were measured under potentiostatic conditions with cathodic polarization of the hydrogen evolution reaction set at -0.1 V . The equilibrium potential was calculated according to the Nernst equation. The amplitude of

Table 1

Chemical compositions of electrolytes used for the deposition of electrocatalytic coatings

Designation of the electrolyte*	Type of solvent	Content of Ni(II) ions, mol/dm^3	Content of Mo(VI), mol/dm^3	Other components and their concentrations, pH
Ni_eth	ethaline	0.25	–	0.5 M $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$
Ni_rel	reline	0.25	–	
Ni-Mo_eth	ethaline	0.25	0.25	
Ni-Mo_rel	reline	0.25	0.25	
Ni_aq	water	1.10	–	250 g/dm^3 $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, 50 g/dm^3 $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ i 30 g/dm^3 H_3BO_3 , pH 4

* – Note: For the sake of convenience, the same conventional electrolyte designations as in the previous work [10] have been used.

the sinusoidal potential component was 0.005 V, and the frequency range was from 0.01 Hz to 100 kHz.

Results and discussion

Quasi-stationary polarization curves for the hydrogen evolution reaction in a 1 M NaOH aqueous alkaline solution on the coatings deposited under the conditions mentioned above (Table 1), as well as the results of their processing in Tafel coordinates, have been previously published elsewhere [10] (Fig. 1 and Table 2, respectively).

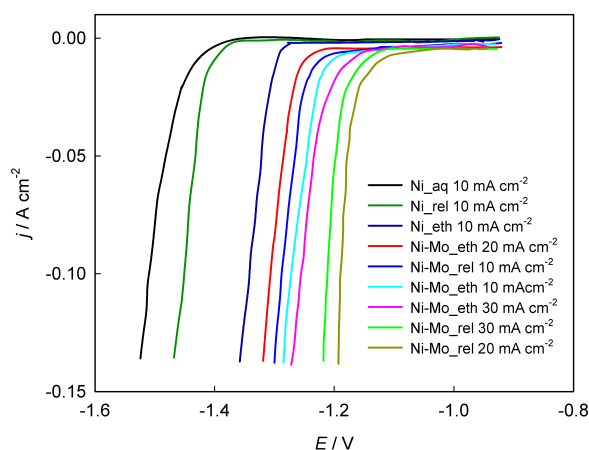


Fig. 1. Polarization curves of hydrogen evolution in a 1 M NaOH aqueous alkaline solution at 298 K on the coatings deposited under the conditions listed in Table 1. Reprinted from [10], Copyright 2023, under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>)

As can be observed, the electrocatalytic activity of the coatings toward the hydrogen evolution reaction correlates well with the molybdenum content: the higher the Mo content, the lower (in magnitude) the Tafel parameter «a» and the higher the exchange current density «j₀». Some variations in the electrocatalyst activity, deposited from solutions based

on ethaline and reline, are attributed to differences in surface morphology characteristics and microstructure features [10].

Thus, the Tafel analysis data indicate an enhanced electrocatalytic activity of Ni-Mo alloys deposited from DES-based electrolytes. To gain a deeper understanding of the observed effects, electrochemical impedance measurements of the cathodic hydrogen evolution reaction on the investigated coatings were conducted (Fig. 2). For better visual perception of the results, the Nyquist plot for the electrocatalyst deposited from the aqueous solution (Ni_{aq}) is separately presented on this figure in a different scale. The analysis of the obtained electrochemical impedance diagrams allows the following conclusions:

(1) The Nyquist plots exhibit a semi-circular shape (or a combination of some semicircles), indicating a hindered charge transfer stage in the electrode reaction. This observation aligns well with the conclusion of the rate-determining Volmer step during hydrogen evolution on electrodeposited Ni and Ni-Mo coatings [10]. Accordingly, the process mechanism can be described as a combination of two consecutive stages:



where H[•] represents a hydrogen atom (intermediate) adsorbed on the active catalytic center of the metal surface.

(2) The semicircles are highly compressed, indicating significant geometric and energetic heterogeneity of the surface [11]. Therefore, for simulating, equivalent circuits should be chosen that include a constant phase element.

Table 2

Results of Tafel analysis of hydrogen evolution reaction occurring on electrocatalytic materials under study (Reprinted with modification from [10], Copyright 2023, under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>))

Electrolyte	Cathode current density, mA cm ⁻²	Content of molybdenum, wt. %	Tafel constants		Exchange current density, j ₀ , A cm ⁻²	Transfer coefficient, α
			-a, V	-b, V dec ⁻¹		
Ni _{aq}	10	–	0.558	0.090	5.94·10 ⁻⁷	0.66
Ni _{rel}	10	–	0.488	0.074	2.63·10 ⁻⁷	0.80
Ni _{eth}	10	–	0.375	0.072	6.17·10 ⁻⁶	0.82
Ni-Mo _{eth}	20	0.05	0.342	0.076	2.98·10 ⁻⁵	0.78
Ni-Mo _{rel}	10	0.26	0.319	0.071	3.38·10 ⁻⁵	0.83
Ni-Mo _{eth}	10	0.26	0.316	0.084	1.64·10 ⁻⁴	0.71
Ni-Mo _{eth}	30	0.51	0.304	0.087	3.36·10 ⁻⁴	0.68
Ni-Mo _{rel}	30	1.55	0.247	0.077	5.98·10 ⁻⁴	0.77
Ni-Mo _{rel}	20	5.28	0.225	0.076	1.11·10 ⁻³	0.78

(3) For hydrogen evolution on coatings deposited from non-aqueous electrolytes (based on DESs), the impedance Nyquist plot consists not of a single semicircle but a combination of several semicircles. Therefore, the electrochemical reaction with a sluggish charge transfer is delocalized across several microdomains of the electrode surface, each differing in nature (chemical composition, microstructure, etc.). Such behavior has been observed in analogous cases and reported in the literature [12,13]. Thus, for the interpretation of electrochemical impedance data measured on the investigated electrocatalysts towards the hydrogen evolution reaction, complex equivalent circuits depicted in Fig. 3 should be applied.

In particular, the scheme shown in Fig. 3a is a modification of the Armstrong-Henderson equivalent circuit developed for electrochemical processes involving adsorbed intermediates [14]. In addition to the solution resistance R_s , charge transfer polarization resistance R_{p1} , and the corresponding constant phase element CPE_1 , denoted here by the subscript «1,» it

additionally includes polarization resistance R_{p2} and constant phase element CPE_2 , corresponding to the elementary charge transfer stage involving adsorbed intermediates. Clearly, such a scheme accurately reflects the physical meaning of the considered process because, due to the presence of the slowed Volmer stage followed by the fast Heyrovsky stage, the hydrogen evolution reaction in an alkaline solution on transition metals involves intermediates. In this case, the presence of two polarization resistances corresponds to two elementary charge transfer stages (involving adsorbed water molecules, i.e., the Volmer stage, and adsorbed hydrogen ad-atoms, i.e., the Heyrovsky stage). This scheme was used to interpret the data obtained on the nickel coating.

However, this scheme proved inadequate for describing the electrochemical impedance measurement data for the hydrogen evolution reaction on nickel-molybdenum alloys, for which a more complex equivalent circuit was proposed (Fig. 3b). It should be noted that this equivalent circuit has been previously

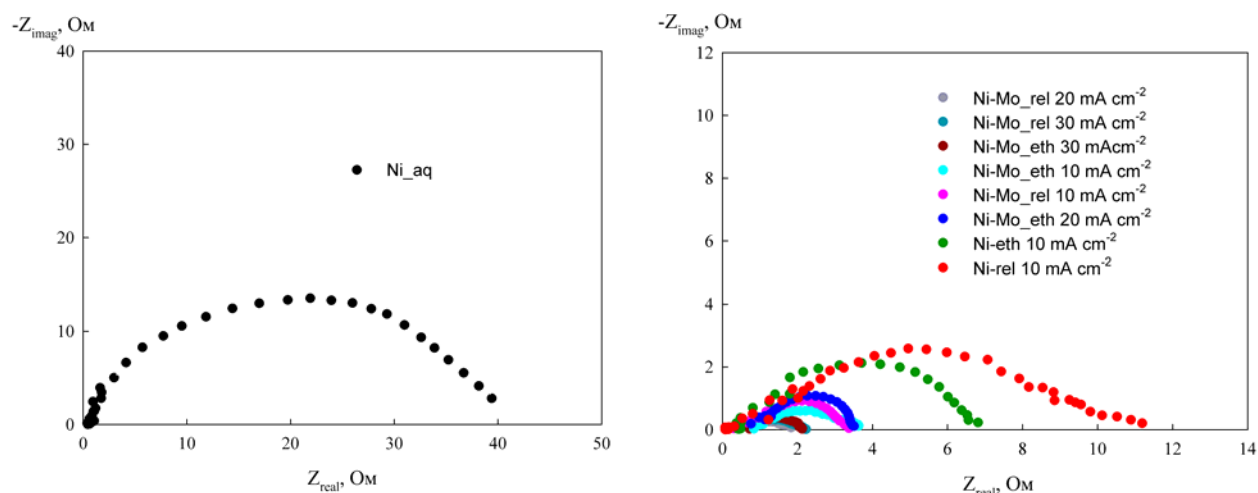


Fig. 2. Electrochemical impedance spectroscopy Nyquist plots for hydrogen evolution in 1 M NaOH at 298 K on the investigated electrode deposited catalysts

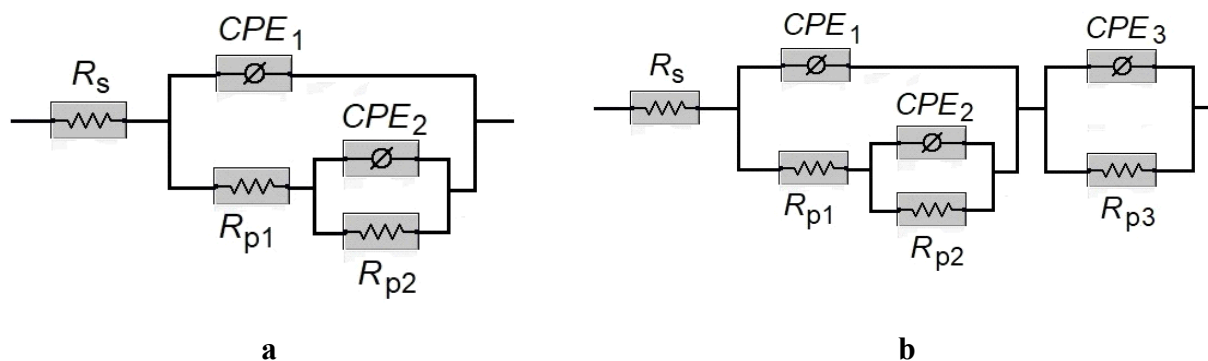


Fig. 3. Equivalent circuits used for simulating the electrochemical impedance

used to simulate the electrochemical impedance of the hydrogen evolution process on nickel-cerium alloy deposited from a DES-based electrolyte [13]. In this equivalent circuit, combinations of elements CPE_1 , R_{p1} , and CPE_2 , R_{p2} , analogous to the scheme in Fig. 3a, relate to the charge transfer stages on a non-uniform metallic surface involving the starting reagent (water molecules) and intermediates (adsorbed hydrogen atoms), respectively. As for the additionally introduced combination of elements CPE_3 and R_{p3} , they might be associated with partial localization of the electrode process in the electrode pores, as suggested in the study [12] (since the electrodeposited coating *a priori* should be considered as a more or less porous material). However, in our opinion, the presence of these elements is more likely due to the partial occurrence of the hydrogen evolution process on «foreign» inclusions in the metallic nickel-containing matrix, which are likely regions of the surface enriched with molybdenum.

The results of calculating the parameter values for the proposed equivalent circuits are summarized in Table 3. It should be noted that each constant phase element is characterized by two quantitative parameters: the capacitance-related constant Q and the dimensionless parameter n , which reflects the degree of surface inhomogeneity of the electrode [11,13]. Here, the impedance of a constant-phase element is determined by the following formula:

$$Z_{CPE} = [Q(j\omega)^n]^{-1}, \quad (3)$$

where Q is the constant related to the capacitive component, j is the imaginary unit ($\sqrt{-1}$), $\omega = 2\pi f$ is the angular frequency, f is the frequency in Hertz, and n is the dimensionless coefficient accounting for surface inhomogeneity.

Analysis of the data in Table 3 allows for the following conclusions:

1. As observed, the data on the electrocatalyst parameters in Table 3 are arranged from top to bottom in the order of decreasing polarization resistance (R_{p1}). This sequence perfectly aligns with the order from Table 2. Therefore, as expected, the value of polarization resistance R_{p1} can be considered a primary measure of electrocatalytic activity, which correlates well with the Tafel parameter «a» determined from polarization curves. Clearly, the lower the value of this polarization resistance, the higher the activity of the considered electrocatalyst. An increase in molybdenum content in the electrocatalytic coating leads to a reduction in polarization resistance R_{p1} .

2. The values of other parameters of individual

components in equivalent circuits do not always monotonically change with an increase in molybdenum content in the coating. In our opinion, the non-monotonicity in the change of various parameters of equivalent circuits with varying molybdenum content in the coating may indicate that the chemical composition of the coating is not the sole factor determining the electrocatalytic behavior. Besides the change in chemical composition, structurally morphological factors, as shown in the previous work [10], are likely to play a crucial role, and they are sensitive to variations in the plating electrolyte composition and electrolysis conditions. Specifically, variations in the deposition current density and the chemical composition of the DES-based electrolyte significantly affect the surface morphology features, crystal lattice parameters, nanocrystal size, and dislocation density. Segregation of the influence of each of these factors on electrocatalytic activity is practically impossible, leading to complex and sometimes ambiguous dependences.

3. Remarkably high values of the parameters Q_1 and Q_2 , *indirectly* characterizing the true surface area available for electrochemical reaction, draw attention. These values, for all coatings deposited from DESs, are significantly higher than for nickel coating produced in a «conventional» aqueous electrolyte. This indicates a highly developed surface area for these deposits, which is extremely favorable for their use as electrocatalysts. As previously mentioned in the literature [15], a highly developed surface of Ni-Mo alloys is one of the reasons for their high activity as catalysts in the electrochemical hydrogen generation.

4. The calculated dimensionless parameters n_1 , n_2 , and n_3 , indicating a significant geometric and energetic heterogeneity of the surface, also point to the substantial non-uniformity of the surface of the investigated electrocatalysts. As known, deviations of these parameters from unity towards smaller values indicate an increase in the degree of microheterogeneity of the electrode surface [11]. The presence of surface microdomains with different types of surface microstructure, distinct crystallographic orientation, varied adsorption energy of starting reagents, intermediates, and reaction products, as well as other differences, is usually a factor contributing to the enhanced electrocatalytic activity.

5. The polarization resistance R_{p2} , corresponding to the charge transfer stage involving intermediates (i.e., adsorbed hydrogen atoms), is significantly lower for the molybdenum-containing coatings than for the coatings that do not contain molybdenum at all. In some cases, the polarization resistance R_{p2} becomes comparable and even smaller than R_{p1} , correlating

with the corresponding decrease in the Tafel slope (Table 2). This may suggest that the kinetic capabilities of the Tafel stage (2) become comparable to the kinetic capabilities of the Volmer stage (1). Such a phenomenon aligns well with established concepts [16,17], indicating that the enhancement of electrocatalytic activity via the formation of nickel-molybdenum alloys occurs due to the formation of a favorable electronic structure, lowering the energy barrier, and accelerating the slowed Volmer stage.

Thus, the data on electrochemical impedance spectroscopy significantly complement and deepen the results of the Tafel analysis of the electrocatalytic behavior of Ni and Ni-Mo coatings, electrodeposited from electrolytes based on deep eutectic solvents.

Conclusions

In this study, a systematic measurement of the electrochemical impedance of the hydrogen evolution reaction in a 1 M NaOH aqueous solution on electrocatalytic coatings of Ni and Ni-Mo deposited from electrolytes based on deep eutectic solvents (DESS) was carried out for the first time. For the interpretation of the obtained data, a modified Armstrong-Henderson equivalent circuit for electrochemical processes involving adsorbed intermediates was proposed. This circuit additionally included a polarization resistance and a constant phase element, taking into account the localization of the electrochemical process on different types of surface microdomains. A correlation between electrocatalytic activity and molybdenum content in the coating was demonstrated. It was established that the main reasons for the improvement of electrocatalytic properties of the coating during the formation of a nickel-molybdenum alloy are an increase in the degree of microheterogeneity of the surface, the development of the surface area available for electrochemical

reaction, and the formation of a favorable electronic structure of the metal, resulting in the acceleration of the slow Volmer stage.

Acknowledgements

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Table 3

Results of calculation of equivalent circuit parameters

Type of coating and current density (mA/cm ²)	R _s , Ω	R _{p1} , Ω·cm ²	Q ₁ , Ω ⁻¹ ·s ^{n₁} ·cm ⁻²	n ₁	R _{p2} , Ω·cm ²	Q ₂ , Ω ⁻¹ ·s ^{n₂} ·cm ⁻²	n ₂	R _{p3} , Ω·cm ²	Q ₃ , Ω ⁻¹ ·s ^{n₃} ·cm ⁻²	n ₃
Ni_aq_10	0.200	62.000	2.840·10 ⁻⁴	0.870	78.800	1.250·10 ⁻³	0.905	–	–	–
Ni_rel_10	0.380	7.720	2.500·10 ⁻²	0.800	16.900	2.510·10 ⁻¹	0.810	–	–	–
Ni_eth_10	1.000	6.200	2.840·10 ⁻³	0.870	18.800	1.250·10 ⁻³	0.965	–	–	–
Ni-Mo_eth_20	0.750	3.984	2.370·10 ⁻²	0.650	0.743	1.385·10 ⁻¹	0.900	0.812	2.868·10 ⁻⁴	0.900
Ni-Mo_rel_10	0.522	3.784	1.346·10 ⁻²	0.570	0.797	5.980·10 ⁻¹	0.969	0.899	2.770·10 ⁻⁴	0.900
Ni-Mo_eth_10	0.256	3.416	1.758·10 ⁻³	0.624	8.396	1.387·10 ⁻²	0.890	1.200	5.153·10 ⁻⁴	0.9009
Ni-Mo_eth_30	0.797	0.840	6.370·10 ⁻³	0.562	3.868	1.768·10 ⁻²	0.758	0.768	2.394·10 ⁻⁴	0.910
Ni-Mo_rel_30	0.810	0.781	3.750·10 ⁻²	0.600	8.800	1.260·10 ⁻²	0.805	1.360	1.125·10 ⁻⁴	0.970
Ni-Mo_rel_20	0.399	0.004	1.547·10 ⁻³	0.870	3.280	5.600·10 ⁻³	0.943	7.824	7.375·10 ⁻⁴	0.951

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ЕЛЕКТРОКАТАЛІТИЧНА ПОВЕДІНКА СПЛАВУ Ni–Mo, ЕЛЕКТРООСАДЖЕНОГО З ЕЛЕКТРОЛІТІВ НА ОСНОВІ НИЗЬКОТЕМПЕРАТУРНИХ ЕВТЕКТИЧНИХ РОЗЧИННИКІВ: ДОСЛІДЖЕННЯ МЕТОДОМ СПЕКТРОСКОПІЇ ЕЛЕКТРОХІМІЧНОГО ІМПЕДАНСУ

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З використанням методу спектроскопії електрохімічного імпедансу здійснено дослідження електрокаталітичної поведінки електроосаджених покриттів Ni і сплаву Ni–Mo у реакції електровиділення водню у водному розчині 1 М NaOH. Для електрохімічного осадження електрокаталітичних покриттів використано електроліти на основі низькотемпературних евтектичних розчинників (евтектичні суміші холін хлориду з етиленгліколем або карбамідом). Для моделювання одержаних годографів імпедансу, що характеризують електрокаталітичну поведінку осаджених покриттів, була використана модифікована еквівалентна схема Армстронга-Гендерсона (Armstrong-Henderson), що передбачає врахування участі у реакції адсорбованих інтермедіатів, і містить три поляризаційних опори та три елементи сталі фази, що дозволяє врахувати локалізацію електрохімічного процесу на різних за природою мікроділянках поверхні. Виявлено, що електрокаталітична активність нікелевих покриттів, осаджених з низькотемпературних евтектичних розчинників, перевищує активність нікелю, одержаного з водного електроліту. Показано, що зростання вмісту молібдену в покритті приводить до підвищення електрокаталітичної активності. Встановлено, що основними причинами покращення електрокаталітичних властивостей покриття при формуванні сплаву Ni з Mo є структурно-морфологічні чинники (зростання ступеня мікротерогенності поверхні і розвинення площі поверхні, доступної для електрохімічної реакції), а також утворення сприятливої електронної структури металу, що приводить до прискорення лімітувальної стадії Фольмера.

Ключові слова: низькотемпературні евтектичні розчинники, електроосадження, сплав нікель-молібден, реакція виділення водню, електрокаталіз, спектроскопія електрохімічного імпедансу.

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ELECTROCATALYTIC BEHAVIOR OF Ni–Mo ALLOY ELECTRODEPOSITED FROM DEEP EUTECTIC SOLVENTS-ASSISTED PLATING BATHS: ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY STUDY

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The electrocatalytic behavior of electrodeposited Ni and Ni–Mo alloy coatings in the hydrogen evolution reaction in a 1 M NaOH aqueous solution was investigated by means of the electrochemical impedance spectroscopy method. The electrochemical deposition of electrocatalytic coatings was carried out using electrolytes based on deep eutectic solvents (eutectic mixtures of choline chloride with ethylene glycol or urea). To simulate the recorded Nyquist plots reflecting the electrocatalytic performance of deposited coatings, a modified Armstrong-Henderson equivalent circuit was employed, which accounts for the involvement of adsorbed intermediates in the reaction. The equivalent circuit included three polarization resistances and three constant phase elements, allowing for the consideration of the localization of the electrochemical process on different surface microdomains. It was found that the electrocatalytic activity of nickel coatings deposited from deep eutectic solvents exceeded the activity of nickel fabricated in an aqueous electrolyte. The increase in molybdenum content in the coating was shown to enhance electrocatalytic activity. It was established that the main reasons for improving the electrocatalytic properties of the Ni–Mo alloy coatings are structural-morphological factors (increase in the degree of microheterogeneity of the surface and the development of the surface area available for electrochemical reaction) and the formation of a favorable electronic structure of the metal, leading to the acceleration of the rate-determining Volmer step.

Keywords: deep eutectic solvents; electrodeposition; nickel-molybdenum alloy; hydrogen evolution reaction; electrocatalysis; electrochemical impedance spectroscopy.

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