FUNCTIONAL PROPERTIES OF NICKEL-BASED ELECTRODEPOSITED COATINGS FOR THE HYDROGEN EVOLUTION REACTION

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Ni–Mo–B coatings with 7–27 wt.% Mo and 0.75–1.36 wt.% B were synthesized electrochemically. SEM, EDX, and titrimetric analyses were revealed their morphology and composition. Corrosion resistance in 1.0 M KOH slightly decreased with higher Mo due to anodic dissolution, yet remained low (0.0035–0.0084 mA/cm²). Catalytic activity depended on Mo content; the best catalyst showed 0.194 V overpotential at 100 mA/cm². Hydrogen evolution followed the Volmer–Heyrovsky mechanism, confirming these coatings' potential for green hydrogen production.

Keywords: electrodeposited Ni–Mo–B coatings, hydrogen, HER, alkaline electrolysis, electrocatalysis, voltammetry, corrosion resistance

Introduction. According to the European Green Deal, fossil fuels are planned to be completely replaced by hydrogen by 2050. Hydrogen can be produced by various methods, with water electrolysis using costly platinum catalysts being the most common. Numerous alternative materials have been proposed to replace platinum. Nickel is an active catalyst for hydrogen generation in alkaline media and can be alloyed with elements such as molybdenum, cobalt, phosphorus, and boron [1]. The Ni–Mo system is considered a promising alternative to platinum catalysts due to its high corrosion resistance, and increasing the molybdenum content reduces the hydrogen evolution overpotential to levels comparable to platinum. Ni–Mo based coatings and alloys are produced by melting or electrodeposition, with the latter being more economical and allowing control over chemical composition and surface morphology by adjusting electrolysis parameters [2]. However, at high molybdenum concentrations, coatings exhibit internal stresses leading to surface cracking, which limits their practical use. To reduce these stresses, heat treatment or the addition of a third component that relaxes stresses is employed. In this study, boron serves as that component. The catalytic activity and corrosion resistance of Ni–Mo–B coatings with varying compositions and surface morphologies for the hydrogen evolution reaction in 1.0 M KOH solution are investigated below.

Materials and methods. Ni–Mo–B coatings were deposited on pretreated copper substrates (polished with 1000 grit SiC paper, washed, degreased with acetone). Electrolysis was performed in a self-regulating electrolyte [2] containing

100 g/L boron suspension at pH 9.0, 60±1 °C, current densities from 0.5 to 10 A/dm², stirring at 300 rpm for 1 hour. A nickel plate was used as the anode.

Electrochemical tests were carried out potentiodynamically (scan rate 1 mV/s) in 1.0 M KOH at 22 °C with argon purging; working electrode area was 0.2 cm². Potentials were referenced to Ag|AgCl|KCl and converted to SHE.

Catalytic activity was evaluated by Tafel parameters, exchange current density, overpotential at 100 mA/cm², and mass transfer coefficient.

Morphology and composition were analyzed by SEM (Zeiss EVO-40XVP) and EDX (Oxford Inca Energy 350). Boron content was determined by titration with 0.1 M NaOH. Surface relief was measured using a "Micron-alpha" interferometric profilometer and roughness by average R_a.

Results and discussion. Chemical analysis (Table 1) revealed that the electrodeposits obtained at different current densities contain nickel, molybdenum, and boron, with no other elements detected. The boron content shows only slight variation across coatings formed at various current densities; however, a clear correlation between its concentration and surface roughness was observed: as the boron content increases within the range of 0.75–1.36 wt.%, the roughness coefficient rises by approximately 28%.

Table 1. Chemical composition and surface roughness of Ni–Mo–B coatings.

Current density, A/dm²	Chemical composition of coatings, wt.%			
	Ni	Mo	B	R_a
0.5	71.85	27.00	1.15	
1.0	78.25	21.00	0.75	2.492
2.5	83.64	15.00	1.36	1.999
5.0	91.00	8.00	1.00	2.775
10.0	92.98	6.00	1.02	2.271

Polarization curves for the cathodic hydrogen evolution reaction on the deposited coatings in 1.0 M KOH are presented in Fig. 2.

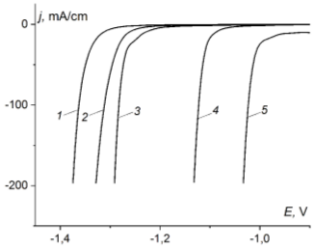

Fig. 1. Cathodic polarization curves for hydrogen ion reduction on molybdenum-containing electrodes with the following molybdenum, wt.%: *1* – 6; *2* – 8; *3* – 15; *4* – 21; *5* – 27.

It was found that the hydrogen evolution overpotential on the electrocatalysts exhibits a clear correlation with the molybdenum content: as the Mo concentration increases from 6.00 to 27.00 wt.%, the overpotential decreases by 0.340 V.

The results of processing the curves shown in Fig. 2 in Tafel coordinates are presented in Table 2. A key indicator of high electrocatalytic activity is the decrease in Tafel slopes *a* and *b*, along with an increase in the exchange current density j_0 for the hydrogen evolution reaction (HER). For the coating containing 6.00 wt.% Mo, the Tafel slope *a* is –0.237 V, *b* is –0.111 V·dec^{-1}, and the exchange current density is 0.007 A/cm². Given that the Tafel slope is close to the theoretical value of 0.118 V·dec^{-1}, it can be concluded that the Volmer step is rate-determining, indicating that hydrogen evolves via a combined Volmer–Heyrovsky mechanism. The transfer coefficient is close to the theoretical value of 0.5. As the Mo content increases, the Tafel slopes decrease, suggesting an enhancement in the kinetics of the HER. Notably, an increase in Mo content from 6.00 to 27.00 wt.% results in approximately a 23-fold increase in the exchange current density. However, the change in chemical composition does not affect the nature of the rate-determining step, and thus, the overall reaction mechanism remains unchanged.

Table 2. Kinetic parameters of the hydrogen evolution reaction on coatings.

Curve number (Fig.2)	η, V (j=100 mA/cm²)	-a, V	- b, V·dec	j_0, A/cm²	α
1	0.554	0.237	0.111	0.007	0.49
2	0.484	0.087	0.079	0.024	0.68
3	0.454	0.093	0.069	0.045	0.78
4	0.294	0.087	0.063	0.042	0.86
5	0.194	0.086	0.108	0.160	0.50

Another important criterion when selecting electrocatalysts for the hydrogen evolution reaction is their durability and stability of the electrode potential over time. Table 3 presents experimental values of the electrode potentials measured at a current density of 100 mA/cm² over a 12-hour period, demonstrating the stable performance of the electrocatalysts under these conditions in alkaline media.

Table 3. Electrocatalyst Potential Values with Varying Molybdenum Content in 1.0 M KOH

wt.% Mo	6	8	15	21	27
Potential, V	-1.38	-1.32	-1.28	-1.12	-1.02

The corrosion resistance of Ni–Mo coatings increases with higher molybdenum content, as evidenced by the decrease in corrosion current density from 0.0055 to 0.0035 mA/cm² (Table 4). This improvement is attributed to the anodic dissolution of molybdenum.

Table 4. Corrosion resistance of coatings in 1.0 M KOH solution.

Ni-Mo			Ni-Mo-B		
wt.% Mo	E_{cor}, -V	i_{cor}, mA/cm^2	wt.% Mo	E_{cor}, -V	i_{cor}, mA/cm^2
2.84	0.49	0.0035	6.00	0.59	0.0036
3.60	0.50	0.0037	8.00	0.56	0.0039
6.50	0.54	0.0042	15.00	0.61	0.0037
13.00	0.57	0.0047	21.00	0.66	0.0050
25.00	0.59	0.0055	28.00	0.68	0.0084

This is accompanied by a shift of the corrosion potential toward more negative values. Additional alloying with boron further shifts the corrosion potentials in the negative direction compared to Ni–Mo coatings, indicating an increase in corrosion rate. This trend is supported by corrosion current densities, which rise slightly—by approximately 1.1 to 1.5 times—at comparable molybdenum content. Such behavior is most likely due to the increase in the specific surface area of the coatings as a result of boron incorporation. The electrochemical corrosion tests demonstrate that the obtained coatings exhibit high corrosion resistance and satisfactory catalytic activity toward the hydrogen evolution reaction. Therefore, they are promising candidates for use as electrodes in alkaline water electrolysis.

Conclusions. Fine-grained, defect-free coatings containing 6–27 wt.% Mo and 0.75–1.36 wt.% B were produced. The coating with the highest molybdenum content demonstrated the best electrocatalytic performance for hydrogen evolution in alkaline medium, with an overpotential of 0.194 V, Tafel slope of 0.108 V·dec^{-1}, and an exchange current density of 0.160 A/cm^2. Although corrosion resistance in 1.0 M KOH slightly decreased with increasing Mo content and additional boron alloying due to anodic dissolution and increased surface area, the corrosion current densities remained low (0.0035–0.0084 mA/cm^2). These properties suggest that the synthesized Ni–Mo–B coatings are highly corrosion-resistant and can be recommended as efficient electrocatalysts for green hydrogen production.

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