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Ni–MoO₂ composite cathodes for hydrogen evolution in alkaline solution. Effect of aging of the electrolyte for their electrodeposition

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Abstract: In this work, the effect of aging of the electrolyte in the electrodeposition of Ni–MoO₂ composite coatings on their morphology (scanning electron microscopy), chemical composition (energy-dispersive X-ray spectroscopy), polarization characteristics and “service life”, tested for the hydrogen evolution reaction (HER) in 32 mass % NaOH at 90 °C, was investigated. Polarization characteristics and results of the “service life” test of Ni–MoO₂ composite coatings obtained after different aging periods of the electrolyte for deposition (suspension of MoO₂ powder particles in a solution containing 2 M NH₄Cl + + 0.2 M NiCl₂) were compared with that recorded for the commercial De Nora’s Ni+RuO₂ cathode coating (DN). It was shown that aging of the electrolyte did not influence the morphology and chemical composition of Ni–MoO₂ composite coatings electrodeposited under conditions simulating their industrial production, while the polarization characteristics for the HER were influenced. The best coating, obtained after 180 days of electrolyte aging, showed a completely different (layered) structure of the deposit and significantly better performance than the commercial DN electrode during the “service life” test.

Keywords: Ni–MoO₂ composite coating; hydrogen evolution; “service life” test.

INTRODUCTION

In the process of chlor–alkali electrolysis for chlorine production in the membrane cells,^{1–3} an ion-exchange membrane separates the anode and the cathode compartments and gaseous hydrogen is produced in the cathode compartment from 30–32 mass % caustic soda solution at a typical operating tempe-

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perature of 90 °C. The efficiency of the cathodes is an important issue in this process, since the overvoltage for the hydrogen evolution reaction (HER) in the cathode compartment contributes significantly to the overall power consumption.³ The efficiency of the cathodes is the result of a combination of certain activities and stability at the high current densities (3–6 kA m⁻²) normally used in technological applications. The main reason for the loss of activity and stability of the cathodes during long-term operation is the so-called “polarity inversion” of the electrodes, which occurs during replacement of old electrodes of an electrolyzer with new ones in the zero-gap cells. During this operation, the anodes and cathodes are short-circuited, causing a reverse current flow that may damage the cathodes and negatively affect their activity for the HER.⁴ Manufacturers can predict how often in a certain period such an operation should be performed and accordingly designed an appropriate accelerated “service life” test for cathodes.^{5,6}

As explained in previous papers,^{6–8} Ni–MoO₂ composite coatings could be electrodeposited from a suspension of MoO₂ powder particles in an electrolyte containing 2M NH₄Cl + 0.2 M NiCl₂ and their overvoltage for the HER could be lower than that on a commercial De Nora’s Ni+RuO₂ cathode obtained under similar conditions of electrolyte circulation and mixing by bubbling gas through the pipes placed on the bottom of the electrolyzer tank.⁷ As was shown,⁷ the optimal content of MoO₂ powder in the electrolyte was 3 g dm⁻³, while the optimal deposition current density was –0.3 A cm⁻². To obtain good quality coating with low overvoltage for the HER, it was necessary to perform the electrodeposition after at least 24 h of conditioning of the prepared suspension, since the suspension needed a certain period to stabilize.⁷

In this work the effect of aging of the electrolyte for electrodeposition of Ni–MoO₂ composite coatings on their morphology, chemical composition, polarization characteristics and “service life” test performance for the HER was investigated and the obtained results were compared with that recorded for the commercial De Nora Ni+RuO₂ cathode coating (DN).

EXPERIMENTAL

HER Investigations

All experiments were performed with extra pure UV water (Smart2PureUV, TKA) and p.a. chemicals in a three compartment electrochemical cell with two Pt mesh counter electrodes placed parallel (in separate compartments) to the working electrode and a saturated calomel electrode (SCE), connected to the working electrode (in the central compartment) by means of a Luggin capillary, as the reference electrode,.

a) *Polarization curve measurements.* The electrodes were first submitted to hydrogen evolution at a constant current density of $j = -0.3 \text{ A cm}^{-2}$ for 0.5 h in 32 mass % NaOH at 90 °C and after such pre-electrolysis, the polarization curves were recorded using a potentiostat Reference 600 and PHE 200 or DC 105 Software (Gamry Instruments). The starting potential was –1.35 V and potential was changed in steps of 0.01 V towards less negative values, up to

the open circuit potential. At each potential, the current response was recorded for 500 s and the value recorded at the end was used to produce the polarization curve. Electrochemical impedance spectroscopy (EIS) measurements were performed at certain potentials in the frequency range from 30 kHz to 1 Hz (*ac* amplitude 0.01 V, EIS 300 Software) and the ohmic resistance (R_{Ω}) was determined from the high-frequency intercept on the Z' axis (the value of R_{Ω} was constant). Each applied potential was corrected for the IR_{Ω} drop and the corresponding polarization curves were plotted.

b) “Service life” test. The experiments were performed in the following way: the electrode was kept at $j = -0.3 \text{ A cm}^{-2}$ for 0.5 h and the corresponding potential response was recorded. Subsequently, the electrode was cycled (5 cycles) in the potential range from -1.25 V to 0.5 V at a sweep rate of 0.05 V s^{-1} . In the next step the electrode was again kept at $j = -0.3 \text{ A cm}^{-2}$ for 500 s and the corresponding potential response was recorded. This procedure was repeated 5 times, until the number of cycles reached 25. The potential response measured at $j = -0.3 \text{ A cm}^{-2}$ for 500 s was corrected for IR_{Ω} drop using the value of ohmic resistance (R_{Ω}) obtained from the EIS measurements. For this test the Ni–MoO₂ coatings (deposited onto Ni 40 mesh) with the best polarization characteristics were used (sample 1 and 5C) and compared with that recorded for the commercial DN electrode under the same conditions (commercial De Nora Ni+RuO₂ coating was originally deposited onto Ni 40 mesh).

Electrodeposition of the Ni–MoO₂ composite coatings

The MoO₂ powder was synthesized by a rheological phase reaction route.^{7,9} All samples were deposited onto Ni 40 mesh from a suspension of MoO₂ powder particles (3 g dm^{-3}) in an electrolyte containing $2 \text{ M NH}_4\text{Cl} + 0.2 \text{ M NiCl}_2$ (pH 3.8) in a pilot plant cell for the deposition of approximately 20 dm^3 (Fig. 1). The electrolyte was circulated with a pump, while the flow rate ($20 \text{ dm}^3 \text{ min}^{-1}$) was measured with a flow meter. Additional mixing of the electrolyte was provided by an airflow of $10 \text{ dm}^3 \text{ min}^{-1}$ through two pipes with small openings facing the bottom of the cell in order to remove eventually precipitated molybdenum oxide particles from the bottom of the cell and force the particles to float and circulate with the electrolyte. The temperature of the electrolyte was kept constant by a thermocouple, heater and control unit (as shown in Fig. 1a). The 40-mesh Ni cathode (dimensions $5 \times 6 \text{ cm}^2$), connected to a Ni holder (frame, Figs. 1b and 1c), was placed between two Ni anode plates ($18 \times 22 \text{ cm}^2$). A home made power supply, with the ripple smaller than 1 %, was used for applying the necessary current/voltage.⁷ In order to examine the influence of electrolyte aging on the morphology, chemical composition and electrochemical properties of the cathodes, samples were deposited from the same electrolyte after 1, 10, 30, 90 and 180 days. Between use, the electrolyte was cycled and mixed every day for at least 1 h.

All Ni 40 mesh substrates were etched only shortly in a 1:3 mixture of H₂O:HNO₃ and washed with distilled water before the deposition of the Ni–MoO₂ composite coatings.

SEM and EDS analysis of the Ni–MoO₂ composite coatings

The appearance of coated surfaces and the cross-sections of the coatings were investigated by scanning electron microscope (SEM) Tescan, VEGA TS 5130 MM equipped with an energy dispersive X-ray spectroscopy (EDS), INCA PentaFET-x3, Oxford Instruments.

Particle size analysis of the suspension containing MoO₂ powder

The average size of MoO₂ powder particles was determined with Brookhaven Instruments light-scattering system equipped with a BI-200SM goniometer, a BI-9000AT correlator, a temperature controller and a Coherent INNOVA 70C argon-ion laser. Dynamic light scattering measurements were performed using 135 mW laser excitation at 514.5 nm at a 90° detection angle.

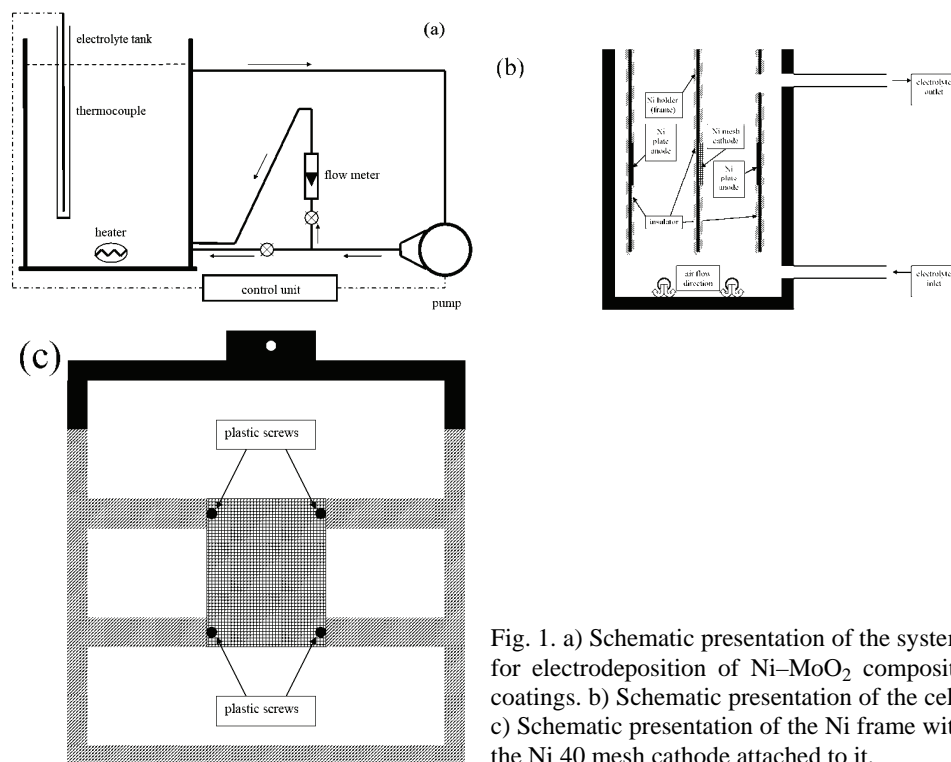


Fig. 1. a) Schematic presentation of the system for electrodeposition of Ni–MoO₂ composite coatings. b) Schematic presentation of the cell. c) Schematic presentation of the Ni frame with the Ni 40 mesh cathode attached to it.

RESULTS AND DISCUSSION

Polarization curves for the HER onto Ni–MoO₂ electrodes

As shown in a previous paper,⁷ the best polarization characteristics were obtained for the sample deposited at -0.3 A cm^{-2} (sample 1). The polarization curves for the HER onto Ni–MoO₂ electrodes obtained after different aging periods (samples 1, 2, 3, 4, 5A, 5B and 5C, see Table I) recorded in 32 mass % NaOH at 90 °C are presented in Fig. 2. All polarization curves are characterized with two slopes: curves 1–3 with $-0.031 \text{ V dec}^{-1}$ in the range of current densities lower than 0.1 A cm^{-2} and -0.13 V dec^{-1} in the range of current densities higher than 0.1 A cm^{-2} ; curve 4 with $-0.038 \text{ V dec}^{-1}$ in the range of current densities lower than 0.1 A cm^{-2} and -0.14 V dec^{-1} in the range of current densities higher than 0.1 A cm^{-2} and sample 5A with $-0.058 \text{ V dec}^{-1}$ in the range of current densities lower than 0.1 A cm^{-2} and -0.14 V dec^{-1} in the range of current densities higher than 0.1 A cm^{-2} (Fig. 2). Such a shape of the polarization curves indicates true catalysis of the HER.^{10–17} Kinetic parameters for the HER, as well as the contribution of surface roughness to the catalytic activity, were evaluated using the EIS technique.⁸ Based on the presented theoretical model for the faradic impedance of the HER,^{10–17} the rate constants of the individual steps

were determined by simulating both the polarization and EIS experimental data. It was found that the reaction proceeded equally *via* the Volmer–Heyrovsky and the Volmer–Tafel routes at lower overpotentials, while at higher overpotentials, the Volmer–Heyrovsky pathway dominated the process with the Heyrovsky step being the rate determining step (rds).⁸ A comparison of the intrinsic activities of the Ni–MoO₂ composite and a flat Ni electrode proved that the combination of Ni and MoO₂ produced a true catalytic effect for the HER.⁸

TABLE I. Conditions of samples deposition and their average chemical compositions obtained by EDS analysis of their cross-sections

Sample deposited after days	Sample No.	j_{dep} A cm ⁻²	τ_{dep} min	d_{av} ^a μm	Position	Composition, at. %		
						O	Ni	Mo
1	1	-0.3	24	56	Average	5	87	8
10	2	-0.3	24	57	Average	5	87	8
30	3	-0.3	24	55	Average	5	87	8
90	4	-0.3	24	54	Average	5	86	9
180	5A	-0.3	24	53	Average	5	84	11
					Mo rich	71	9	20
	5B	-0.1	10	15	Ni rich	4	89	7
					Mo rich	71	9	20
5C	-0.062	15	23	Ni rich	4	86	10	

^aAverage thickness was estimated from the SEM cross-sections

As can be seen from Fig. 2, during the first 30 days of electrolyte aging (samples 1–3), no change in the polarization characteristics for the HER could be observed. Simultaneously, practically no change was observed in the thicknesses and compositions of the coatings, Table I. After 90 days of electrolyte aging, the polarization curve for the HER changed, showing more positive potential values in the range of low current densities and slightly higher slope at high current densities (Fig. 2, curve 4) in comparison with samples 1, 2 and 3. A significant change in the activity for the HER was recorded for the sample deposited from the same electrolyte (under the same conditions, deposition current density -0.3 A cm^{-2}) after an aging period of 180 days (sample 5A) at current densities higher than 0.03 A cm^{-2} . Although the chemical composition and thickness, as well as the appearance of the coating surface, did not change, the overvoltage for the HER increased by about 50 mV. Such an effect could be the consequence of agglomeration of the MoO₂ powder particles. The morphology of sample 5A is presented in Fig. 3. The same morphologies were obtained for samples 1–4. As can be seen on the back-scatter SEM of the cross-section of sample 5A (Fig. 3b), the coating is characterized with gray and white areas, the former corresponding to Ni-richer deposits and the latter corresponding to the Mo-richer deposits.^{6–8} Unfortunately, agglomerates in the composite coating were not detectable. The agglomeration of MoO₂ powder particles was confirmed by particle size analysis

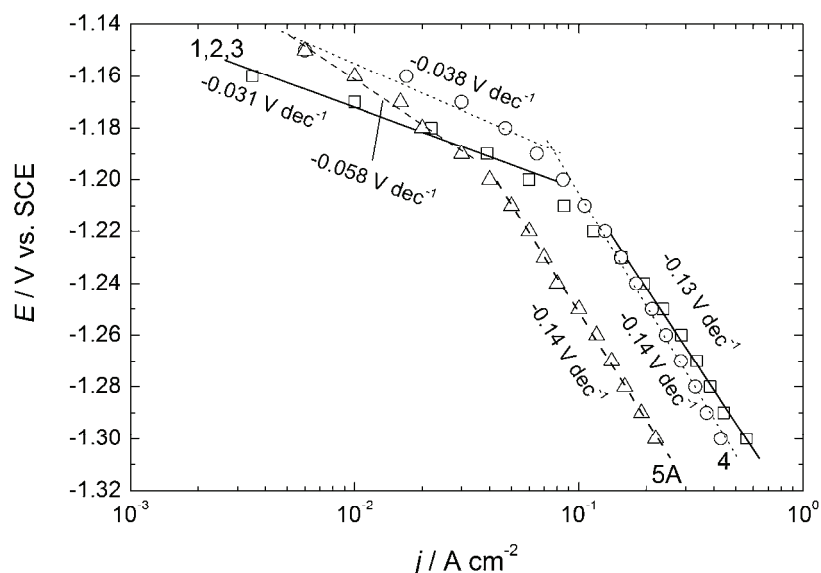


Fig. 2. Polarization curves for the HER on Ni–MoO₂ cathode coatings recorded in a solution of 32 mass % NaOH at 90 °C. The Ni–MoO₂ coatings were deposited from a suspension containing 3 g dm⁻³ MoO₂ powder particles in 2 M NH₄Cl + 0.2 M NiCl₂ electrolyte, pH 3.8, after different times of electrolyte aging: 1 – after 1 day (□); 2 – after 10 days (□); 3 – after 30 days (□); 4 – after 90 days (○) and 5A – after 180 days (△).

(see Experimental). For samples deposited after 1, 10 and 30 days, average particles size in the electrolyte was about 200 nm, while in the electrolyte used for deposition after 180 days, average particles size was about 500 nm. It appears that with increasing size of the MoO₂ powder particles (due to agglomeration), the applied current density of -0.3 A cm^{-2} for sample deposition was not the optimal one and that for a given hydrodynamics an optimal value of the deposition current density should be defined by additional experiments. Accordingly, two samples, 5B and 5C, were deposited at lower current densities of -0.1 A cm^{-2} and -0.062 A cm^{-2} , respectively. Polarization curves for HER for samples 5A–5C are presented in Fig. 4 together with that for the commercial DN electrode. As can be seen, a significant decrease in the overvoltage for HER was achieved with the decreases in the deposition current density. The potential for the HER recorded at -0.3 A cm^{-2} (current density in industrial electrolysis) amounted to: -1.34 V for sample 5A, -1.27 V for sample 5B and -1.20 V for sample 5C (for the DN electrode this value was -1.23 V). Hence, it appears that sample 5C required a lower overvoltage for the HER by about 30 mV compared to that that for the commercial DN electrode. By the SEM and EDS analysis of the surfaces and the cross-sections of the samples 5A, 5B and 5C, it was discovered that their surfaces and the cross-sections were different. The morphology and chemical composition of the sur-

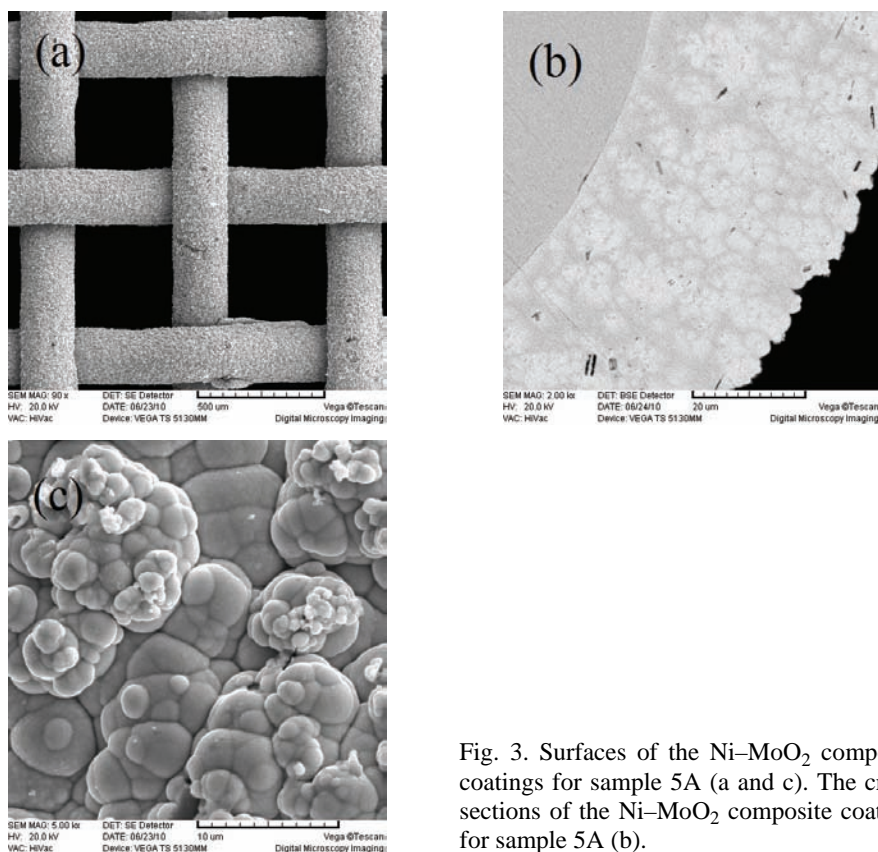


Fig. 3. Surfaces of the Ni-MoO₂ composite coatings for sample 5A (a and c). The cross-sections of the Ni-MoO₂ composite coatings for sample 5A (b).

face of sample 5A was identical to those for samples 1–4 (Figs. 3a and 3c). The cross-section analysis also showed practically the same results (Fig. 3b and Table I). In the case of sample 5B, the SEM analysis of its surface showed the presence of small number of cracks, while EDS analysis confirmed that the surface was composed of a Ni-rich coating. The cross-section analysis showed a layered structure, Fig. 5b, with the top layer being rich in Ni and the bottom layer of the coating being rich in Mo. Average chemical compositions of these layers are given in Table I. In the case of sample 5C, the surface was characterized by the presence of larger number of cracks, Fig. 6a. Simultaneously, the surface was rougher than those for samples 1–4, 5A and 5B (Fig. 3c), as shown in Fig. 6c. EDS analysis of the surface of 5C showed that the top layer was rich in Mo. Its cross-section analysis also showed a layered structure with a much lower number of thicker layers, only three Mo-rich and three Ni-rich layers (Fig. 6b). In this case, the top layer was rich in Mo, while the bottom layer was rich in Ni. Taking into account that coatings richer in Mo are better catalysts for the HER, it is quite clear why its polarization curve showed a lower overvoltage for the HER for

about 70 mV than that for the sample 5B at the same current density usually used in industrial electrolysis ($j = -0.3 \text{ A cm}^{-2}$).

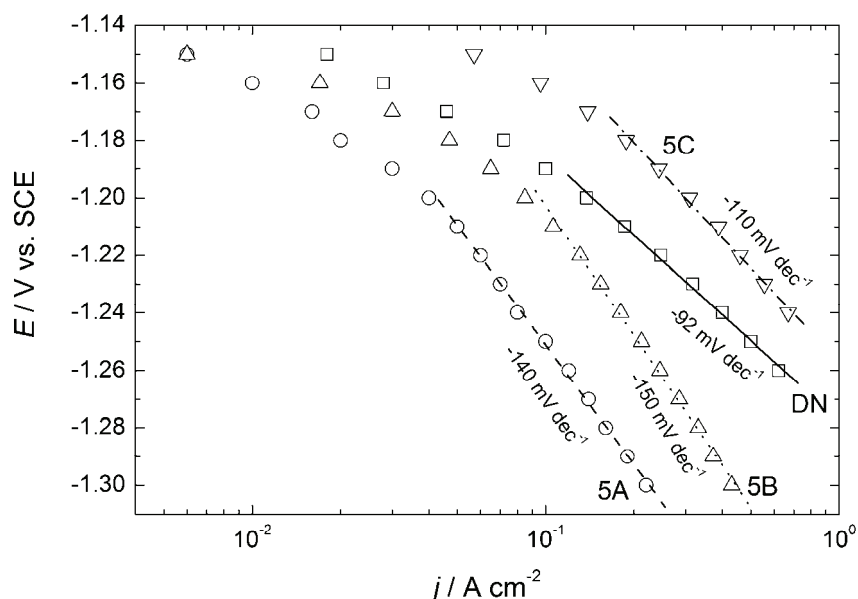


Fig. 4. Polarization curves for the HER on Ni-MoO₂ cathode coatings recorded in a solution of 32 mass % NaOH at 90 °C. The Ni-MoO₂ coatings were deposited from a suspension containing 3 g dm⁻³ MoO₂ powder particles in 2 M NH₄Cl + 0.2 M NiCl₂ electrolyte, pH 3.8, after 180 days of electrolyte aging: (○) 5A – $j_{\text{dep}} = -0.3 \text{ A cm}^{-2}$; (△) 5B – $j_{\text{dep}} = -0.1 \text{ A cm}^{-2}$; and (▽) 5C – $j_{\text{dep}} = -0.062 \text{ A cm}^{-2}$. For comparison, the polarization curve for the commercial De Nora electrode (DN – □), recorded under the same conditions, is presented.

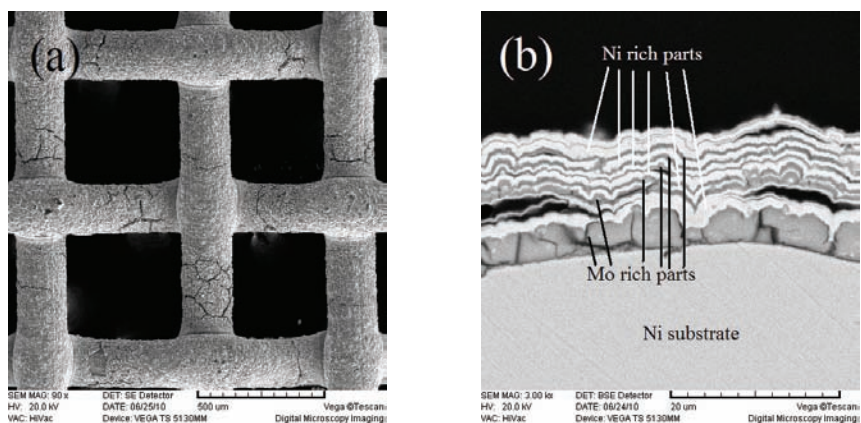


Fig. 5. Surface (a) and cross-section (b) of the Ni-MoO₂ composite coating for sample 5B (SEM). The average chemical compositions of the Ni-rich and Mo-rich layers (EDS) are given in Table I.

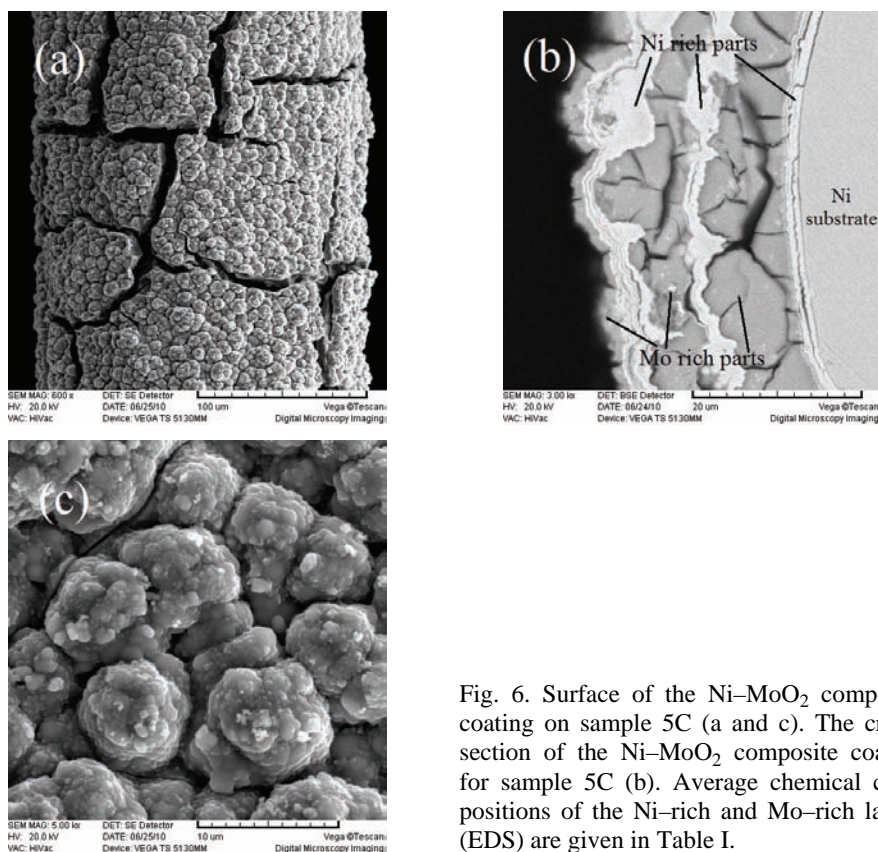


Fig. 6. Surface of the Ni–MoO₂ composite coating on sample 5C (a and c). The cross-section of the Ni–MoO₂ composite coating for sample 5C (b). Average chemical compositions of the Ni-rich and Mo-rich layers (EDS) are given in Table I.

“Service life” test

After recording the polarization curves, the electrodes 1, 5C and DN were subjected to the “service life” test, as explained in the Experimental section. Since in most industrial plants, automatic cathodic protection of cathodes is switched on during shut-downs, the “service life” test is designed to estimate the efficiency of cathodes during so-called “polarity inversion” which occurs during the replacement of old electrodes of an electrolyzer with new ones in the zero-gap cells (see Introduction). In a previous paper,⁶ it was shown that the activity of Ni–MoO₂ and DN electrodes at the end of the “service life” test dropped to approximately 54 % of the initial value, being comparable with the results obtained for Pt-based cathodes.⁵ The SEM–EDS analysis of the Ni–MoO₂ electrode (sample 1) after the “service life” test showed that parts of their surfaces rich in Mo had peeled off during the cycling treatment of this electrode. It was concluded that the dissolution of MoO₂-rich parts of the coating occurred at anodic potentials, causing the loss of their activity for the HER.⁶

The results of the “service life” test for electrodes 1, 5C and DN are presented in Fig. 7. The potentials for the HER, recorded at $j = -0.3 \text{ A cm}^{-2}$, before and after a certain period of cycling the electrodes (from -1.25 to 0.5 V at a sweep rate of 0.05 V s^{-1}), indicate that sample 1 and DN behaved in a similar manner. With increasing number of cycles, the potential response changed to more negative values, starting from about -1.21 V and finishing at about -1.24 V . In the case of sample 5C, the starting potential was more positive, about -1.20 V , and had not changed after 10 cycles. With further increase of the number of cycles, the potential decreased to about -1.21 V after 25 cycles. Hence, it appeared that the most stable electrode during the “service life” test was sample 5C. Considering its structure (cross-section analysis) and the fact that practically no changes on the electrode surface before and after the “service life” test could be detected by SEM analysis (contrary to the sample 1), it is most likely that the second layer from the top of the coating, rich in Ni (Fig. 6b) protected further decomposition of the coating (after the first layer, rich in Mo, has been dissolved during oxygen evolution at anodic potentials, as it was the case with the sample 1 in a previous study⁶), causing much better stability of this coating during the “service life” test.

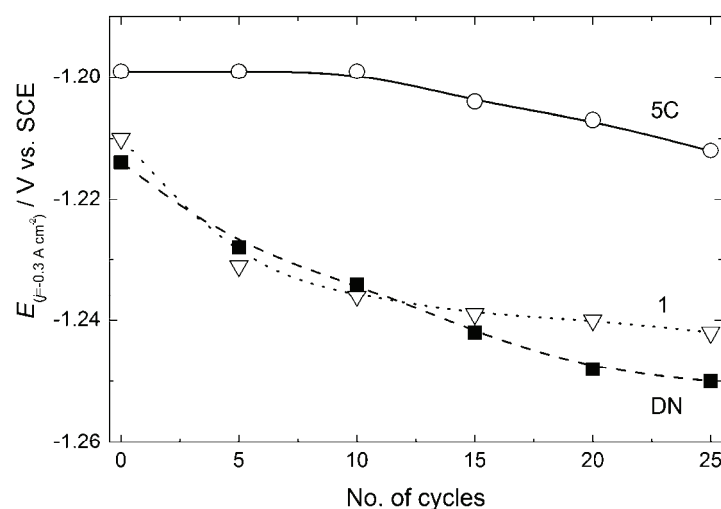


Fig. 7. Potentials for the HER corrected for the IR_{Ω} drop, recorded at $j = -0.3 \text{ A cm}^{-2}$, as a function of the number of cycles performed in the potential range from -1.25 to 0.5 V at a sweep rate of 0.05 V s^{-1} , for samples 1 and 5C and the commercial DN electrode (“service life” test).

CONCLUSIONS

From the results presented in this study, it could be concluded that the morphology and chemical composition of the Ni–MoO₂ coatings deposited under the

same conditions (current density and hydrodynamics) remained practically constant after 180 days of aging of the electrolyte for their deposition, although agglomeration of the MoO₂ powder particles was found to occur. Contrarily, the polarization curves for the HER on these coatings were different, showing an increase in the overvoltage with aging time. After 180 days of electrolyte aging and significant agglomeration of MoO₂ powder particles, a different morphology and chemical composition of the coatings were obtained at lower deposition current densities. The overvoltage for the HER on these coatings decreased due to the change in the morphology and chemical composition. The “service life” test for the electrode with the best polarization characteristics showed that this electrode would be more stable during industrial application than the commercial De Nora Ni+RuO₂ electrode.

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ИЗВОД

КОМПОЗИТНЕ Ni-MoO₂ КАТОДЕ ЗА ИЗДВАЈАЊЕ ВОДНИКА ИЗ АЛКАЛНИХ РАСТВОРА. ЕФЕКАТ СТАРЕЊА ЕЛЕКТРОЛИТА ЗА ЊИХОВО ТАЛОЖЕЊЕ

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У овом раду испитиван је утицај старења електролита за електрохемијско таложење Ni-MoO₂ композитних превлака на њихову морфологију (скенирајућа електронска микроскопија), хемијски састав (енергетско-дисперзиона анализа X-зрацима), поларизационе карактеристике и тест стабилности у условима индустријске примене за издвајање водоника у раствору 32 мас. % NaOH на 90 °C. Остварени резултати су упоређени са резултатима за комерцијалну катоду Ni+RuO₂, произвођача “De Nora”. Показано је да старење електролита (суспензија MoO₂ честица у електролиту састава 2 M NH₄Cl + 0,2 M NiCl₂) не утиче на морфологију и хемијски састав Ni-MoO₂ композитних превлака исталожених у условима њихове индустријске производње иако долази до агломерације честица MoO₂, али значајно утиче на поларизационе карактеристике за реакцију издвајања водоника. Електрода са најбољим поларизационим карактеристикама за реакцију издвајања водоника, исталожена из електролита старог 180 дана при мањим густинама струје од оптималне за свеж електролит, показала је значајно боље перформансе (бољу стабилност) од комерцијалне катоде при испитивању теста стабилности у условима индустријске примене.

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