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EXTENDED ABSTRACT

**Electrodeposition and characterization of Ni–MoO<sub>2</sub> composite coatings as cathodes for the hydrogen evolution reaction in alkaline solution\***

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*Abstract:* Composite Ni–MoO<sub>2</sub> coatings were prepared and characterized with respect to their possible application as electrocatalysts for the hydrogen evolution reaction (HER) in alkaline solution. The composites were electrodeposited onto Ni meshes from an ammonium chloride Ni solution with suspended MoO<sub>2</sub> particles under simulated industrial conditions for the production of commercial cathodes. The influence of the concentration of MoO<sub>2</sub> particles in the solution and deposition current density on the morphology, and chemical and phase composition of the obtained coatings were investigated by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD). Catalytic activity of the coatings for the HER was examined by polarization measurements in a 32 wt. % NaOH solution at 90 °C and compared to the activity of the commercial *De Nora's* cathode (DN). It was shown that the most active Ni–MoO<sub>2</sub> coating exhibited better polarization characteristics for the HER than the DN cathode. The mechanism of the HER on the specified Ni–MoO<sub>2</sub> coating was investigated in 8 mol dm<sup>-3</sup> NaOH at 30 °C by means of steady-state polarization measurements and an electrochemical impedance spectroscopy (EIS). Based on the theoretical interpretation of the experimental data, the rate constants of the three individual steps of the HER were determined and the source of catalytic activity of the coating was elucidated.

*Keywords:* hydrogen evolution; electrocatalysis; Ni–MoO<sub>2</sub> coating; morphology; electrochemical impedance spectroscopy.

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Chlor-alkali electrolysis is an industrial process of major importance since more than 95 % of chlorine and 99.5 % of sodium hydroxide are annually produced in the world by mercury, diaphragm and membrane chlor-alkali technologies.<sup>1</sup> One of the main obstacles to the future development of the chlor-alkali industry is the high cost of the consumed electrical energy,<sup>1</sup> partially associated with the inadequate efficiency of the hydrogen-evolving cathodes. Over the past years, great effort has been devoted to searching for cathode materials suitable for industrial application,<sup>2–16</sup> which have to meet several criteria, such as: high catalytic activity for the hydrogen evolution reaction (HER), large surface area, good mechanical, chemical and corrosion stability and low cost of the components. Nickel is used as the basic component of industrial cathodes due to its stability in alkaline media, moderate activity for the HER and low price.<sup>17</sup> In commercial zero-gap membrane cells of the *Industrie De Nora* (DN), a Ni–RuO<sub>2</sub> composite coating, characterized by the low overpotential for the HER, is employed as the cathode. However, regarding a high price of ruthenium compounds on the market, economic factors promote the tendency to replace the Ru-containing cathode with materials based on non-noble metals that show similar catalytic activity for the HER in alkaline solution as the commercial cathode.

In this lecture, the results of an investigation of the microstructure, chemical and phase composition and catalytic activity for the HER of Ni–MoO<sub>2</sub> composite coatings prepared by the simultaneous electrodeposition of Ni and MoO<sub>2</sub> were presented. The coatings were electrodeposited from suspensions composed of 0.2 mol dm<sup>-3</sup> NiCl<sub>2</sub> + 2.0 mol dm<sup>-3</sup> NH<sub>4</sub>Cl solution (pH 3.6) and MoO<sub>2</sub> particles.<sup>10</sup> The average particle size of MoO<sub>2</sub> powder was determined to be 850 nm using the Scherrer formula.<sup>10</sup> The electrodeposition was performed in a test cell,<sup>9</sup> *i.e.*, a 20 dm<sup>3</sup> volume flow reactor, in which the suspension was circulating with a constant flow rate of 50 L min<sup>-1</sup> and air bubbles were continually introduced at the bottom of the cell in order to prevent precipitation of the suspended MoO<sub>2</sub> particles and achieve their additional mixing. A Ni mesh 40 was used as the cathode substrate, while the anodes were two Ni plates. Dimensions of all three electrodes were 18 cm×22 cm. The catalytic activities of the obtained Ni–MoO<sub>2</sub> coatings were estimated by recording steady-state polarization curves for the HER in a 32 wt. % NaOH solution at 90 °C, and compared to the activity of the commercial DN electrode. The morphology, chemical and phase composition of the coatings were investigated by SEM, EDS and XRD analysis, respectively.

In order to establish the optimal conditions for the electrodeposition of Ni–MoO<sub>2</sub> coatings, preliminary experiments were conducted in a beaker cell ( $V = 0.5$  dm<sup>3</sup>) with much smaller electrodes (2 cm×3 cm).<sup>10</sup> The concentration of MoO<sub>2</sub> particles in the solution was varied in the range of 3–10 g dm<sup>-3</sup>, whereas the deposition current density  $j_{\text{dep}}$  was varied from 50–1000 mA cm<sup>-2</sup>. It was found that the coatings with larger content of Mo, electrodeposited from sus-

pensions with higher concentration of MoO<sub>2</sub> and at lower  $j_{\text{dep}}$ , exhibited the best catalytic activity for the HER, but were also characterized by the appearance of cracks and smaller and non-uniform thickness, implying a short service life under industrial conditions of exploitation. On the other hand, the coatings with a lower content of Mo, *i.e.*, a larger content of Ni, were thicker and had a developed surface area, but the overpotential for the HER was considerably larger. With respect to the catalytic activity for the HER, it appeared that for every applied  $j_{\text{dep}}$ , there is an optimal concentration of MoO<sub>2</sub> particles in the solution and *vice versa*.

Deposition of the coatings in the test cell was carried out at  $j_{\text{dep}} = -300 \text{ mA cm}^{-2}$ , while the concentration of MoO<sub>2</sub> was varied in the range of  $1 - 3 \text{ g dm}^{-3}$ .<sup>10</sup> It was discovered that the morphology and composition of the Ni-MoO<sub>2</sub> coatings and, consequently, their activity for the HER, were crucially dependent on conditioning time of the deposition suspension. The coating electrodeposited from the suspension with  $2 \text{ g dm}^{-3}$  of MoO<sub>2</sub>, conditioned for 1 h, was  $2 \text{ }\mu\text{m}$  thick and characterized by the presence of cracks and a uniform composition with 16 at. % Mo and 62 at. % O. The coating electrodeposited from the same suspension after 24 h conditioning had a thickness of about  $40 \text{ }\mu\text{m}$  and was composed of uniformly distributed Ni-rich (practically pure Ni) and MoO<sub>2</sub>-rich (16 at. % Mo) parts, distinguishable from back-scatter electron micrographs of the cross section as the gray and white areas, respectively. The difference in the microstructure and composition of the two coatings was attributed to the sluggish occlusion of suspended MoO<sub>2</sub> particles by Ni<sup>2+</sup> in the solution. The latter coating displayed a 60 mV lower overpotential for the HER at higher current densities compared to the former one.

The best polarization characteristics in 32 wt. % NaOH at 90 °C exhibited by the coating, deposited from a suspension with  $3 \text{ g dm}^{-3}$  of MoO<sub>2</sub> after 24 h conditioning.<sup>10</sup> At a current density of  $-300 \text{ mA cm}^{-2}$ , the overpotential for the HER recorded on this sample was 15 mV lower in comparison to that of the commercial DN cathode. Its surface was found to be composed of two characteristic parts,<sup>18</sup> differing in composition and morphology. The Ni-rich parts (78. at. % Ni) consisted of agglomerates of ball-like grains of  $2 \text{ }\mu\text{m}$  in diameter, whereas the MoO<sub>2</sub>-rich parts (76 at. % O) were characterized by the presence of mud-like cracks typical for electrodeposited Ni-Mo-O systems.<sup>19,20</sup> Cross section analysis of MoO<sub>2</sub>-rich parts revealed that the cracks did not reach the Ni substrate, but extended only to the compact Ni-rich underlayer. Only two phases, Ni and MoO<sub>2</sub>, were detected by XRD analysis, confirming that the MoO<sub>2</sub> particles were incorporated into the Ni matrix during the electrodeposition process. It was concluded that the coating prepared from the suspension containing  $3 \text{ g dm}^{-3}$  of MoO<sub>2</sub> after 24 h of aging represents the most promising candidate for replacement of the commercial DN cathode since it exhibits better polarization characteristics for the HER than the DN cathode and has a satisfactory microstructure.

The kinetics and mechanism of the HER on this coating were examined in an 8 mol dm<sup>-3</sup> NaOH solution at 30 °C by means of steady-state polarization measurements and the electrochemical impedance spectroscopy (EIS).<sup>18</sup> The polarization curve was characterized by only one well-defined Tafel slope of  $b = -122$  mV dec<sup>-1</sup> in the overpotential range  $|\eta| \geq 70$  mV. The impedance spectra recorded at four different overpotentials corresponding to the Tafel region consisted of two overlapped semicircles on the complex plane diagrams. The so-called 1CPE equivalent circuit<sup>21,22</sup> was successfully fitted to the impedance spectra, providing the values for the circuit parameters. Based on the theoretical model for the HER,<sup>23,24</sup> the polarization curve and the overpotential dependences of the circuit parameters were simultaneously simulated using the non-linear least squares method. The fitting procedure produced values of the rate constants of the three elementary steps of the HER. In the range of low overpotentials,  $0 < |\eta| < 50$  mV, the rates of the Heyrovsky and Tafel steps were approximately the same, indicating that the reaction equally proceeds through both possible reaction pathways, the Volmer–Heyrovsky and the Volmer–Tafel. At  $|\eta| > 150$  mV, the rate of the Tafel step was approaching the limiting value and the reaction dominantly proceeded through the Volmer–Heyrovsky reaction pathway, with the Heyrovsky step being the rate determining one.<sup>18</sup>

At the most negative overpotential studied by EIS, the roughness factor was calculated to be 125. In order to separate the contribution of surface roughness to the catalytic activity for the HER, the intrinsic activity of examined Ni–MoO<sub>2</sub> coating was determined and compared to the intrinsic activity of a flat polycrystalline Ni electrode reported in literature.<sup>25,26</sup> Considering that the intrinsic activity for the Ni–MoO<sub>2</sub> electrode was an order of magnitude higher in comparison with the one for a polycrystalline Ni, it was concluded that the synergetic effect on the catalytic activity for the HER in alkaline solution could be assigned to a Ni + MoO<sub>2</sub> combination.

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## ИЗВОД

ЕЛЕКТРОХЕМИЈСКО ТАЛОЖЕЊЕ И КАРАКТЕРИЗАЦИЈА КОМПОЗИТНИХ Ni-MoO<sub>2</sub> ПРЕВЛАКА КАО КАТОДА ЗА РЕАКЦИЈУ ИЗДВАЈАЊА ВОДОНИКА У АЛКАЛНИМ РАСТВОРИМА

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Композитне Ni-MoO<sub>2</sub> превлаке су припремљене и окарактерисане са становишта њихове могуће примене као катализатора за реакцију издвајања водоника у алкалним растворима. Композити су електрохемијски исталожени на Ni мрежице из амонијум-хлоридног раствора никла са суспендованим MoO<sub>2</sub> честицама у симулираном индустријским условима за производњу комерцијалних катода. Утицај концентрације честица MoO<sub>2</sub> у раствору и густине струје таложења на морфологију и хемијски и фазни састав добијених превлака испитиван је методама скенирајуће електронске микроскопије, енергетски дисперзивне спектроскопије X-зрачења и рендгенске дифракције. Каталитичка активност превлака за издвајање водоника испитивана је поларизационим мерењима у 32 мас. % NaOH на 90 °C и упоређена са активношћу комерцијалне катоде (De Nora). Најактивнија Ni-MoO<sub>2</sub> превлака показује боље поларизационе карактеристике него комерцијална катода. Механизам издвајања водоника на наведеној Ni-MoO<sub>2</sub> превлаци у 8 mol dm<sup>-3</sup> NaOH на 30 °C испитан је помоћу стационарних поларизационих мерења и методе спектроскопије електрохемијске импеданције. На основу теоријске интерпретације експерименталних података одређене су вредности константи брзина појединачних ступњева реакције и разјашњена природа каталитичке активности превлаке.

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## REFERENCES

1. T. F. O'Brien, T. V. Bommaraju, F. Hine, *Handbook of Chlor-Alkali Technology, Volume I: Fundamentals*, Springer Science + Business Media, Inc., New York, USA, 2005, pp. 37-47
2. I. Arul Raj, K. I. Vasu, *J. Appl. Electrochem.* **22** (1992) 471
3. L. B. Albertini, A. C. D. Angelo, E. R. Gonzalez, *J. Appl. Electrochem.* **22** (1992) 888
4. J. Divisek, H. Schmitz, B. Steffen, *Electrochim. Acta* **39** (1994) 1723
5. J. Fournier, H. Menard, L. Brossard, *J. Appl. Electrochem.* **25** (1995) 923
6. Th. Borucinsky, S. Rausch, H. Wendt, *J. Appl. Electrochem.* **27** (1997) 762
7. R. K. Shervedani, A. R. Madram, *Electrochim. Acta* **53** (2007) 426
8. A. L. Antozzi, C. Bargioni, L. Iacopetti, M. Musiani, L. Vasquez-Gomez, *Electrochim. Acta* **53** (2008) 7410
9. N. V. Krstajić, Lj. Gajić-Krstajić, U. Lačnjevac, B. M. Jović, S. Mora, V. D. Jović, *Int. J. Hydrogen Energy* **36** (2011) 6441
10. N. V. Krstajić, U. Lačnjevac, B. M. Jović, S. Mora, V. D. Jović, *Int. J. Hydrogen Energy* **36** (2011) 6450
11. U. Č. Lačnjevac, V. D. Jović, B. M. Jović, *Zaštita materijala* **52** (2011) 153
12. V. D. Jović, U. Lačnjevac, B. M. Jović, Lj. Karanović, N. V. Krstajić, *Int. J. Hydrogen Energy* **37** (2012) 17882
13. V. D. Jović, U. Lačnjevac, B. M. Jović, N. V. Krstajić, *Electrochim. Acta* **63** (2012) 124

14. B. M. Jović, U. Č. Lačnjevac, V. D. Jović, Lj. M. Gajić-Krstajić, N. V. Krstajić, *J. Serb. Chem. Soc.* **77** (2012) 211
15. V. D. Jović, U. Č. Lačnjevac, B. M. Jović, Lj. M. Gajić-Krstajić, N. V. Krstajić, *J. Serb. Chem. Soc.* (2012), doi: 10.2298/JSC120831112J.
16. G. Tasić, B. Jović, U. Lačnjevac, N. Krstajić, V. Jović, *J. Electrochem. Sci. Eng.* **3** (2013) 29
17. M. Wang, Z. Wang, Z. Guo, Z. Li, *Int. J. Hydrogen Energy* **36** (2011) 3305.
18. U. Č. Lačnjevac, B. M. Jović, V. D. Jović, N. V. Krstajić, *J. Electroanal. Chem.* **677–680** (2012) 31.
19. U. Lačnjevac, V. D. Jović, B. M. Jović, Z. Baščarević, M. G. Pavlović, *Zaštita materijala* **49** (2008) 41.
20. U. Lačnjevac, B. M. Jović, Z. Baščarević, V. M. Maksimović, V. D. Jović, *Electrochim. Acta* **54** (2009) 3115.
21. C. Hitz, A. Lasia, *J. Electroanal. Chem.* **500** (2001) 213.
22. L. Birry, A. Lasia, *J. Appl. Electrochem.* **34** (2004) 735.
23. R. D. Armstrong, M. Henderson, *J. Electroanal. Chem.* **39** (1972) 81.
24. D. A. Harrington, B. E. Conway, *Electrochim. Acta* **32** (1987) 1703.
25. A. Lasia, A. Rami, *J. Electroanal. Chem.* **294** (1990) 123.
26. N. V. Krstajić, M. Popović, B. Grgur, M. Vojnović, D. Šepa, *J. Electroanal. Chem.* **512** (2001) 16.