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Determination of kinetic parameters for the hydrogen evolution reaction on the electrodeposited Ni–MoO_2 composite coating in alkaline solution

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ABSTRACT

As a result of research on the non-noble metal-based composite electrocatalysts for the hydrogen evolution reaction (HER), the Ni–MoO_2 composite coating was produced by electrodeposition from an NH_4Cl and $NiCl_2$ containing solution with suspended MoO_2 powder particles, exhibiting almost the identical activity for the HER as the commercial cathode in conditions of industrial application and satisfactory mechanical stability. In this work, investigations were extended to the kinetics and mechanism of the HER on the Ni–MoO_2 electrode in 8 M NaOH solution at 30 °C. The steady-state polarization curve for the HER was characterized by only one Tafel slope of −122 mV/dec. Kinetic parameters for the HER, as well as a contribution of surface roughness to the catalytic activity, were evaluated using an electrochemical impedance spectroscopy (EIS) technique. On the basis of the presented theoretical model for the faradaic impedance of the HER, the rate constants of the individual steps were determined by simulating both polarization and EIS experimental data. It was found that the reaction equally proceeds via the Volmer–Heyrovsky and Volmer–Tafel routes at lower overpotentials, while at higher overpotentials the Volmer–Heyrovsky pathway dominates the process with the Heyrovsky step being the rate determining step (*rds*). A comparison of intrinsic activities of the Ni–MoO_2 composite and a flat Ni electrode proved that the combination of Ni and MoO_2 produced a true catalytic effect for the HER.

1. Introduction

Chlor-alkali electrolysis is of major industrial importance since more than 95% of chlorine and 99.5% of NaOH in the world are annually produced by the three chlor-alkali technologies [1]. Beside the environmental concerns and market demands, the future development of chlor-alkali industry is principally dictated by the high cost of consumed electrical energy [1], partially determined by the large overpotential for the hydrogen evolution reaction (HER) proceeding on the cathode. Although hydrogen is not considered a primary product in the process, in order to reduce the energy costs as much as possible, great effort has been devoted to searching for material for the HER appropriate for industrial exploitation, which has to meet several criteria, such as: high catalytic activity for the HER, a large real surface area, a low cost of the electrode components, good mechanical properties and high corrosion stability during the long-term electrolysis as well as during the electrolysis shut-downs when the reverse polarity of electrodes may occur [2–4]. The best known electrocatalysts for the HER are the platinum group metals [5], but they are not economically acceptable for large-scale industrial application due to their limited resources and, consequently, high price. Among the non-noble metals, nickel has been regarded as the reference material for the HER cathode against which performance of all other synthesized materials may be compared [5], owing above all to its good corrosion resistance in concentrated alkaline solution, relatively good activity and low price [2]. Nickel has been widely used in the investigated multi-component cathode materials, mostly in combination with P, S, Al, Zn, Fe, Co, Cr, W and Mo [6–8]. Jakšić [9] showed that the alloying of Ni and Mo could lead to substantial improvement of the catalytic activity for the HER. The kinetics and mechanism of the HER in alkaline solution were investigated on Ni–Mo based alloys prepared metallurgically [10,11], deposited by vacuum plasma spraying [7,12] or pressed and heated [7] with subsequent leaching of active components, or obtained by mechanical alloying [13], but most studies were focused on Ni–Mo alloys electrodeposited under various operating conditions [4,14–28]. Lowering of the overpotential for the HER observed with the electrodeposited alloys was principally attributed to an increase in real surface area.

The enhanced catalytic properties for the HER were reported for Ni–Mo based composite coatings prepared by incorporation of Mo-containing particles during electrodeposition of nickel from suitable baths [29,30]. Kubisztal et al. [30] studied the HER on the Ni coating containing embedded Mo powder particles. They

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showed that the increase of Mo in the composite to 28–36 wt.% produced 3–6 times larger intrinsic activity in comparison with a pure Ni matrix, along with a considerable increase in surface roughness and porosity. Castro et al. [29] investigated the mechanism of the HER on the electrodeposited Ni/NiMoS$_2$ composite electrode by modeling the recorded impedance diagrams and concluded that the enhanced catalytic activity could be assigned to both an increased active surface area and synergetic effects.

In our previous works, we deposited Ni–MoO$_x$ composites from a Watts bath with suspended MoO$_3$ particles [31] and Ni–MoO$_2$ composites from an ammonium chloride Ni bath with suspended MoO$_2$ particles [32] onto the Ni mesh, and tested their activity for the HER in 32 wt.% NaOH at 90 °C. At the current density of 300 mA cm^{-2}, corresponding to the industrial conditions of chlor-alkali electrolysis, the best Ni–MoO$_x$ and Ni–MoO$_2$ coatings possessed almost the same overpotential for the HER as De Nora's commercial Ni + RuO$_2$ (DN) cathode [32]. In the "service life" test that was based on monitoring the current density response of electrodes after the repetitive cycling between the range of potentials corresponding to hydrogen and oxygen evolution both the coatings showed the loss of activity comparable to that of the DN electrode [33]. However, the Ni–MoO$_x$ coating, which had been characterized by large cracks reaching the substrate, was almost completely removed from the Ni mesh after the test. In contrast to that, only thin, cracked parts of the Ni–MoO$_2$ coating located at crossings of the two Ni wires were peeled off during the test, while most of the coating was preserved. Since these results indicated the Ni–MoO$_2$ composite coating as the most promising replacement for the commercial DN cathode, it was involved in further kinetics analysis.

The aim of the present work was to investigate the mechanism of the HER on the most active Ni–MoO$_2$ electrode in 8 M NaOH solution at 30 °C by means of steady-state polarization measurements and an electrochemical impedance spectroscopy (EIS) technique. From the theoretical interpretation of results, rate constants of the reaction steps were determined and sources of the apparent activity were elucidated.

2. Theoretical background

The mechanism of the HER in aqueous alkaline solution is commonly represented as a combination of three elementary reactions, involving electrochemical adsorption of an H atom (the Volmer step)

$$M + H_2O + e^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MH_{ads} + OH^- \tag{1}$$

followed by electrochemical desorption (the Heyrovsky step)

$$MH_{ads} + H_2O + e^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} M + H_2 + OH^- \tag{2}$$

and/or chemical recombination of H atoms (the Tafel step)

$$MH_{ads} + MH_{ads} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} 2M + H_2 \tag{3}$$

where k_i and k_{-i} are the rate constants of the forward and backward reactions. Assuming that the Langmuir adsorption isotherm can be applied, the reaction rates of the corresponding steps are given by

$$\begin{aligned} v_1 &= k_1(1-\theta)\exp\left(-\frac{\beta_1 F\eta}{RT}\right) - k_{-1}\exp\left[\frac{(1-\beta_1)F\eta}{RT}\right] \\ &= k'_1(1-\theta) - k'_{-1}\theta = v_{V,c} - v_{V,a} \end{aligned} \tag{4}$$

$$\begin{aligned} v_2 &= k_2\theta\exp\left(-\frac{\beta_2 F\eta}{RT}\right) - k_{-2}(1-\theta)\exp\left[\frac{(1-\beta_2)F\eta}{RT}\right] \\ &= k'_2\theta - k'_{-2}(1-\theta) = v_{H,c} - v_{H,a} \end{aligned} \tag{5}$$

$$v_3 = k_3\theta^2 - k_{-3}(1-\theta)^2 = v_{T,c} - v_{T,a} \tag{6}$$

Surface concentrations of the adsorbed reaction intermediate H$_{ads}$ and the unoccupied adsorption sites at the electrode are given in the rate law equations as surface coverage fractions θ and $(1-\theta)$, respectively. The chemical rate constants have been written to include concentrations of OH$^-$ and H$_2$O in the solution and the partial pressure of H$_2$, which are approximated to remain constant during a reaction. The symmetry factors of electrochemical steps (β_1 and β_2) are generally independent parameters, but it can be reasonably assumed that $\beta_1 = \beta_2 = \beta = 0.5$ for elementary reactions. The rates of the forward and backward reactions of the three elementary steps are represented with v_c and v_a, respectively.

At equilibrium conditions ($\eta = 0$) reaction rates are equal to zero ($v_1 = v_2 = v_3 = 0$) and the following relationships between $k_{\pm i}$ can be derived:

$$k_{-2} = \frac{k_1 k_2}{k_{-1}} \tag{7}$$

$$k_{-3} = \frac{k_1^2 k_3}{k_{-1}^2} \tag{8}$$

Taking into account Eqs. (7) and (8), the number of independent rate constants is reduced from six to four.

The charge balance under a steady-state current density, j, and the mass balance of the intermediate H$_{ads}$ are respectively given by the following equations

$$r_0 = \frac{j}{F} = -(v_1 + v_2) \tag{9}$$

$$r_1 = \frac{q_1}{F}\left(\frac{d\theta}{dt}\right) = v_1 - v_2 - 2v_3 \tag{10}$$

where r_0 is the net rate of consumption of electrons (r_0 negative for cathodic current), r_1 is the accumulation rate of H$_{ads}$ at the surface and q_1 is the charge necessary for complete coverage of the electrode surface by adsorbed H.

At steady-state conditions the accumulation term in Eq. (10) is equal to zero ($r_1 = 0$) and the steady-state coverage θ can be expressed by

$$\theta = \frac{-(k'_1 + k'_{-1} + k'_2 + k'_{-2} + 4k_{-3}) + \sqrt{(k'_1 + k'_{-1} + k'_2 + k'_{-2} + 4k_{-3})^2 + 8(k_3 - k_{-3})(k'_1 + k'_{-2} + 2k_{-3})}}{4(k_3 - k_{-3})} \tag{11}$$

Armstrong and Henderson [34] and Harrington and Conway [35] provided the theoretical considerations concerning the faradaic impedance for the HER, Z_f. Assuming that $j = j(\eta, \theta)$ and the system may be regarded linear for a small applied amplitude of η, after expansion of Eqs. (9) and (10) to the first order Taylor series and subsequent Fourier transforms Z_f can be expressed by

$$\frac{1}{Z_f} = \frac{1}{R_{ct}} + \frac{1}{R_0(1 + i\omega\tau)} \tag{12}$$

where the kinetic parameters R_{ct}, R_0 and τ are defined as:

$$\frac{1}{R_{ct}} = F\left(\frac{\partial r_0}{\partial \eta}\right)_\theta = \frac{F^2\beta}{RT}[k'_1(1-\theta) + k'_{-1}\theta + k'_2\theta + k'_{-2}(1-\theta)] \tag{13}$$

$$\begin{aligned} \frac{1}{R_0} &= \frac{F^2\tau}{q_1}\left(\frac{\partial r_0}{\partial \theta}\right)_\eta \left(\frac{\partial r_1}{\partial \eta}\right)_\theta \\ &= \frac{F^2\beta}{RT}\frac{[-k'_1(1-\theta) - k'_{-1}\theta + k'_2\theta + k'_{-2}(1-\theta)](k'_1 + k'_{-1} - k'_2 - k'_{-2})}{k'_1 + k'_{-1} + k'_2 + k'_{-2} + 4k_3\theta + 4k_{-3}(1-\theta)} \end{aligned} \tag{14}$$

$$\frac{1}{\tau} = -\frac{F}{q_1}\left(\frac{\partial r_1}{\partial \theta}\right)_\eta = \frac{F}{q_1}[k'_1 + k'_{-1} + k'_2 + k'_{-2} + 4k_3\theta + 4k_{-3}(1-\theta)] \tag{15}$$