

Waldfried Plieth · George S. Georgiev

The Markov chain model of alloy electrodeposition: application to NiCo and NiMo

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Abstract The Markov chain model of alloy deposition was applied to cobalt–nickel. The characteristic parameters of the model are the g_i values describing the selectivity of the deposition process for its components. The values recently determined for Co and Ni (g_{Co} and g_{Ni}) depend on the current density. This could be quantitatively described by the mass transport limitation for Co. The model was also applied to the nickel–molybdenum system, an example for induced co-deposition. Data published by Podlaha and Landolt [4, 5] could be described by the equation

$$\frac{x_{\text{Ni}}}{x_{\text{Mo}}} = \frac{g_{\text{Ni}} \frac{c_{\text{Ni}}}{c_{\text{Mo}}} + c_{\text{Ci}}^n}{c_{\text{Ci}}^n},$$

where x_{Ni} and x_{Mo} are the mole fractions in the alloy, c_{Ni} and c_{Mo} the concentrations (in mol dm^{-3}) in the electrolyte, and c_{Ci} is the concentration of citrate used as catalyst in the system. The g_{Ni} factor was determined and the dependence on current density and electrolyte convection could be quantitatively described.

Introduction

Established models exist for the description of the electrochemical deposition of pure metals. For alloys the selection rules of the surface for the components and the rules determining the structure of the alloy are much less clear. Recently a concept was suggested which should provide a better understanding of alloy deposition [1, 2]. Various kink site positions are defined

for an alloy surface. Residence times of the alloy atoms in the different kink site positions provide an image of why the alloy is deposited in the observed form. It was shown that in a first approximation, values for the residence time could be calculated with the simple assumption that the activation energy of the separation of an atom from the kink site position is proportional to the bond energies of the bonds broken in the separation process. The kink site positions are occupied in an alternative manner by the different components of the alloy. For the description of this selection process the Markov chain model, used for the description of the formation of copolymers of different monomers, was adapted to the alloy deposition [3]. Equations were derived describing the influence of different parameters on the electrochemical reactions. In a first application of the model, the deposition of CoNi alloys could be described.

In the present paper the principal equations of the Markov chain model will be repeated and for the first time mass transport will be included into the model. To test the model on a more complicated system the induced co-deposition of Mo with Ni is analyzed. An equation is derived describing quantitatively the experimental results published by Podlaha and Landolt [4, 5].

The principal background of the model

In the process of formation of a crystalline phase of a bi-component alloy AB, two kink site positions A^* and B^* can react with the two kinds of ions in the electrolyte to form the following new kink site positions: atom A surrounded by atom B (AB^*); atom B surrounded by atom A (BA^*); atom A surrounded by atom A (AA^*) and atom B surrounded by atom B (BB^*). With the asterisk the atoms most recently accumulated on the kink site positions are denoted (Fig. 1).

The kinetic model of residence times [1, 2] provides an explanation of the history of these kink site positions.

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W. Plieth (✉)
University of Technology Dresden, 01062 Dresden, Germany

G. S. Georgiev
Faculty of Chemistry, University of Sofia, 1 I Boucher Avenue,
1164 Sofia, Bulgaria

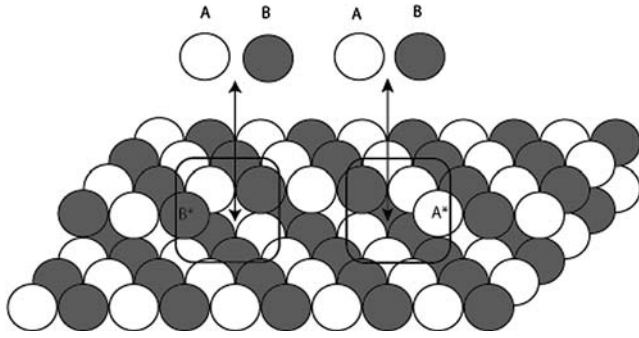
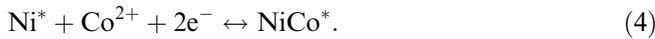
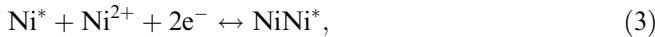
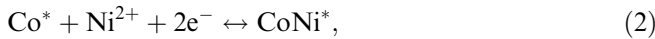
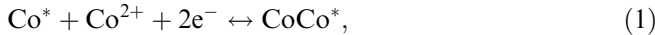


Fig. 1 Different kink site positions A^* and B^* in alloy deposition (areas in the frames). Atoms in kink site positions can react with ions A or B of the electrolyte forming one of four kink site positions AA^* , AB^* , BA^* , BB^*

However, the residence time has to be compared with the concentration of atoms in the electrolyte layer adjacent to the surface and available for accumulation on the kink site position. In the most simple case equilibrium conditions between these concentrations and the atoms in the kink site positions can be assumed. The cobalt–nickel alloy is used as an example. This is a very simple electrochemical alloy system of so called anomalous co-deposition of Co with Ni, equal size of atoms (atomic radius of Ni 0.124 nm, of Co 0.125 nm [6]) and complete miscibility in the crystal. Then the elementary kink site transformations for alloy crystallization can be represented by the following four equilibrium reactions



These equations describe in a schematic manner the equilibrium between the atoms in the kink site positions and in the electrolyte without any details about the intermediate steps. The surface density of the principal four kink site positions (in square brackets) is related to the ion concentration of the two components Co and Ni in the electrolyte layer adjacent to the surface, described by c_{Co} and c_{Ni}

$$[\text{CoCo}^*] = K_{\text{CoCo}} \exp\left(-\frac{2F\Delta E}{RT}\right) [\text{Co}^*] c_{\text{Co}}, \quad (5)$$

$$[\text{CoNi}^*] = K_{\text{CoNi}} \exp\left(-\frac{2F\Delta E}{RT}\right) [\text{Co}^*] c_{\text{Ni}}, \quad (6)$$

$$[\text{NiNi}^*] = K_{\text{NiNi}} \exp\left(-\frac{2F\Delta E}{RT}\right) [\text{Ni}^*] c_{\text{Ni}}, \quad (7)$$

$$[\text{NiCo}^*] = K_{\text{NiCo}} \exp\left(-\frac{2F\Delta E}{RT}\right) [\text{Ni}^*] c_{\text{Co}}. \quad (8)$$

The exponential term describes the potential dependence of the equilibrium. ΔE , in principle the potential drop across the interface, is in practice the potential difference between the electrode and an arbitrary reference electrode.

It is possible to express the conditional probabilities p_{ij} (i, j for Ni, Co, respectively) for both conservation and alteration of the active atom (denoted by asterisks) in each elementary crystallization step (1–4):

$$p_{\text{CoCo}} = \frac{[\text{CoCo}^*]}{[\text{CoCo}^*] + [\text{CoNi}^*]}, \quad (9)$$

$$p_{\text{CoNi}} = \frac{[\text{CoNi}^*]}{[\text{CoCo}^*] + [\text{CoNi}^*]} = 1 - p_{\text{CoCo}}, \quad (10)$$

$$p_{\text{NiNi}} = \frac{[\text{NiNi}^*]}{[\text{NiNi}^*] + [\text{NiCo}^*]}, \quad (11)$$

$$p_{\text{NiCo}} = \frac{[\text{NiCo}^*]}{[\text{NiNi}^*] + [\text{NiCo}^*]} = 1 - p_{\text{NiNi}}. \quad (12)$$

The probability can be expressed by the equilibrium constants and ion concentrations in the electrolyte bath by insertion of the relations (5–8) for the active atoms in the kink site positions in Eqs. 9–12:

$$p_{\text{CoCo}} = \frac{g_{\text{Co}} c_{\text{Co}}}{g_{\text{Co}} c_{\text{Co}} + c_{\text{Ni}}}, \quad (13)$$

$$p_{\text{CoNi}} = \frac{c_{\text{Ni}}}{g_{\text{Co}} c_{\text{Co}} + c_{\text{Ni}}}, \quad (14)$$

$$p_{\text{NiNi}} = \frac{g_{\text{Ni}} c_{\text{Ni}}}{g_{\text{A}} c_{\text{Ni}} + c_{\text{Co}}}, \quad (15)$$

$$p_{\text{NiCo}} = \frac{c_{\text{Co}}}{g_{\text{Ni}} c_{\text{Ni}} + c_{\text{Co}}}, \quad (16)$$

with

$$g_{\text{Co}} = \frac{K_{\text{CoCo}}}{K_{\text{CoNi}}}, \quad (17)$$

$$g_{\text{Ni}} = \frac{K_{\text{NiNi}}}{K_{\text{NiCo}}}, \quad (18)$$

g_{Co} and g_{Ni} are the ratios of the corresponding equilibrium constants of the competing elementary reactions. The potential dependence of the single equilibrium constants is eliminated if the ratios in the g_i values are formulated. The g_i values represent the selectivity of the kink site positions on the surface for Co or Ni, respectively.

The kink site transformations can be treated as a finite Markov chain. Each active atom in the kink site position (A^* , B^*) corresponds to the same Markov chain state (A^* , B^*). This is in accordance with the above mentioned kink site peculiarity that the last atom added to it determines the nature and activity of the kink site position. Then the probabilities defined above form the Markov chain transition matrix

$$P = \begin{bmatrix} p_{CoCo} & p_{CoNi} \\ p_{NiCo} & p_{NiNi} \end{bmatrix}. \quad (19)$$

From the finite Markov chain theory [12] it follows that the elements of the eigenvector ($\alpha = (\alpha_{Co}, \alpha_{Ni})$) of matrix P ($\alpha P = \alpha$) are the atomic fractions (x_{Co} and x_{Ni}) of atoms Co and Ni in the produced alloy.

$$\alpha_{Co} = x_{Co} = \frac{p_{NiCo}}{p_{NiCo} + p_{CoNi}} \quad (20)$$

$$\alpha_{Ni} = x_{Ni} = \frac{p_{CoNi}}{p_{NiCo} + p_{CoNi}}. \quad (21)$$

By substitution of the probabilities in Eqs. 20, 21 by Eqs. 14, 16 the following equation is derived:

$$\frac{x_{Co}}{x_{Ni}} = \frac{p_{NiCo}}{p_{CoNi}} = \frac{c_{Co}}{c_{Ni}} \frac{g_{Co}c_{Co} + c_{Ni}}{g_{Ni}c_{Ni} + c_{Co}}. \quad (22)$$

Equation 22 can be transformed into linear forms and g_{Co} and g_{Ni} can be determined from the intercepts and slopes of the experimental straight lines. Introducing the substitutions

$$v = \frac{x_{Co}}{x_{Ni}} \quad \text{and} \quad w = \frac{c_{Co}}{c_{Ni}},$$

the following two equations are derived

$$\frac{v-1}{w} = g_{Co} - \frac{v}{w^2} g_{Ni} \quad (23)$$

or

$$w \left(1 - \frac{1}{v} \right) = -g_{Ni} + \frac{w^2}{v} g_{Co}. \quad (24)$$

For the experimental determination of the g_i values ($i = Co, Ni$) the experimental dependence of the alloy composition on the ion concentration in the electrolyte must be known.

For the CoNi alloy data were published in Refs. [7, 8]. They are represented in the form $v = x_{Co}/x_{Ni}$ versus $w = c_{Co}/c_{Ni}$ in Fig. 2. From linear plots of these data using Eq. 23 or 24 the g_i values were obtained. Figures 3 and 4 show g_i values as a function of the applied deposition current density.

The data in Fig. 2 are represented for 5, 10 and 15 A dm⁻². Also, the g_i values in Figs. 3 and 4 depend on the current density. Changing the current density will have two effects: (1) diminishing the concentration of ions at the electrode surface because a diffusion profile will be built up; and (2) changing the overpotential. It will be shown that the dependence of the experimental results on the current density can be explained quantitatively by the influence of the mass transport.

It was pointed out that in the equilibrium formulated in Eqs. 5–8 the concentrations of metal ions in the electrolyte layer adjacent to the metal surface are used. For mass transport controlled processes this surface

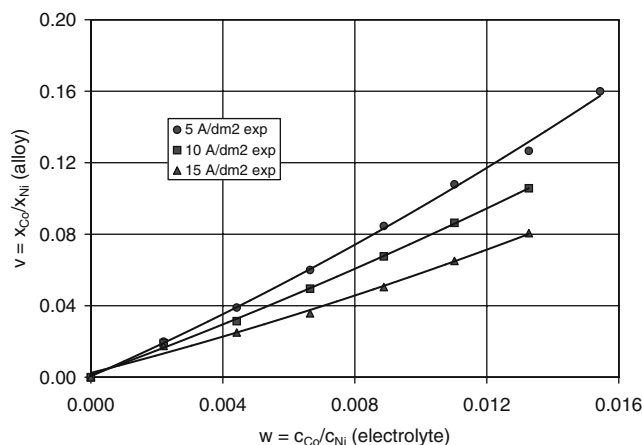


Fig. 2 The mole fraction $v = x_{Co}/x_{Ni}$ of electroplated CoNi alloys as a function of the concentration ratio $w = c_{Co}/c_{Ni}$ in concentrated Ni sulfamate electrolytes (500–600 g/l Ni sulfamate, 5–15 g/l Ni chloride, 35–45 g/l boric acid) at three current densities ($i = 5 \text{ A dm}^{-2}$ (circles, curve 1), $i = 10 \text{ A dm}^{-2}$ (squares, curve 2) and $i = 15 \text{ A dm}^{-2}$ (triangles, curve 3); solid lines represent the trend of the data; temperature: 70 °C, pH = 4 [7, 8])

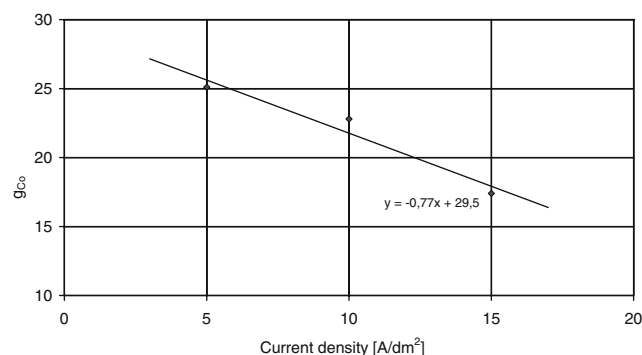


Fig. 3 g_{Co} values as a function of current density; the g_{Co} values characterizes the CoNi alloy selectivity for Co; Co–Ni sulfamate electrolyte, $T = 70 \text{ °C}$, pH = 4 [7, 8]

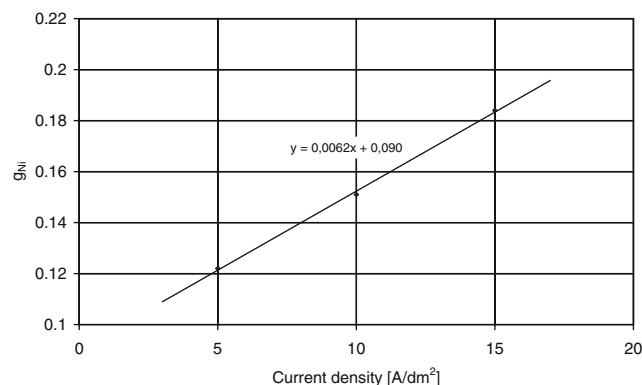


Fig. 4 g_{Ni} values as a function of current density; the g_{Ni} values characterize the CoNi alloy selectivity for Ni; Co–Ni sulfamate electrolyte, $T = 70 \text{ °C}$, pH = 4 [7, 8]

concentration of metal ions depends on the current density. The large concentration of nickel will not depend on mass transport limitations, that is $c_{\text{Ni}} = c_{0,\text{Ni}}$. However, the small concentration of Co near the surface will differ from the bulk concentration $c_{0,\text{Co}}$. Mass transport by stationary diffusion is usually described by the equation

$$i = -k_{\text{dif}}(c - c_0), \quad (25)$$

where c_0 represents the bulk concentration and $k_{\text{dif}} = 2FD/\delta$ contains the Faraday constant, Diffusion coefficient and the thickness of the Nernst diffusion layer. One obtains for c

$$c = c_0(1 - k^*i). \quad (26)$$

The constant k^* stands for $k^* = 1/(c_{0,\text{Co}} k_{\text{dif}})$. Inserting Eq. 26 for the Co concentration into the ratio $w = c_{\text{Co}}/c_{\text{Ni}}$ gives

$$w = w_0(1 - k^*i) \quad (27)$$

with $w_0 = c_{0,\text{Co}}/c_{0,\text{Ni}}$. Then the linearized Eq. 23 obtains the form

$$\frac{v-1}{w_0} = g_{\text{Co}}^*(1 - k^*i) - \frac{v}{w_0^2} \frac{g_{\text{Ni}}^*}{1 - k^*i}. \quad (28)$$

For $k^*i \ll 1$ this equation can be approximated by

$$\frac{v-1}{w_0} = g_{\text{Co}}^*(1 - k^*i) - \frac{v}{w_0^2} g_{\text{Ni}}^*(1 + k^*i). \quad (29)$$

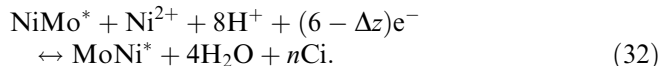
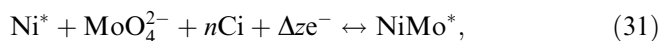
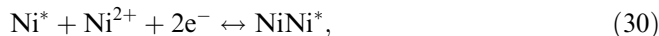
The experimental values of g_{Co} and g_{Ni} confirm this current dependence. Thus g_{Co} is decreasing with increasing current while g_{Ni} is increasing with increasing current in accordance with the experimental observation of Figs. 3 and 4. Extrapolation to zero current allows the determination of g_i^* values corrected for mass transport: $g_{\text{Co}}^* = 29.5$ and $g_{\text{Ni}}^* = 0.090$. The slope of Fig. 3 is $g_{\text{Co}}^* k^* = 0.77 \text{ dm}^2 \text{ A}^{-1}$, and the slope of Fig. 4 is $g_{\text{Ni}}^* k^* = 0.0062 \text{ dm}^2 \text{ A}^{-1}$. The values of k^* calculated from the slopes are $k^* = 0.069$ and $0.026 \text{ dm}^2 \text{ A}^{-1}$. Taking an average value of k^* and a mean value of the concentration of $c_{0,\text{Co}} = 0.01 \text{ mol/dm}^3$ (the concentration in the experimental region varied between 0.03 and 0.004 mol/dm^3), a mean value of $k_{\text{dif}} = 7.5 \text{ dm A}^{-1} \text{ mol}^{-1}$ is obtained. With $k_{\text{dif}} = 2FD_{\text{Co}}/\delta$ this gives a value $D_{\text{Co}}/\delta = 3.9 \times 10^{-5} \text{ dm s}^{-1}$. With D_{Co} of the order of $10^{-9} \text{ dm}^2 \text{ s}^{-1}$, a value of the thickness of the Nernst diffusion layer δ of the order of $0.26 \times 10^{-4} \text{ dm} = 2.6 \times 10^{-3} \text{ cm}$ is obtained.

The peculiarity revealed by the analysis is the selectivity for Co, the slightly more electronegative element.

Induced deposition: NiMo

The NiCo alloy is a simple system with complete miscibility. To test the model on a more sophisticated system, the nickel–molybdenum system was chosen with

components of different size (atomic radius of Ni 0.124 nm, of Mo 0.140 nm [6]) and so called induced co-deposition of molybdenum. This system was intensively investigated and was most recently studied by Podlaha and Landolt [4, 5]. The deposition reactions according to the model of alternating kink site positions can be formulated by the following equations



NiMo* stands for a schematic complex $[\text{Ni-MoO}_4(\text{Ci})_n]^{(2+\Delta z)-}$.

Reaction 31 takes into account the catalytic activity of citrate and a partial discharge of the molybdenum in the NiMo–citrate complex, representing the NiMo* kink site position.

Experimental evidence shows that no reaction of NiMo* with MoO_4^{2-} is possible. The kink site position MoMo* does not exist.

Then the following probabilities can be formulated

$$p_{\text{NiNi}} = \frac{[\text{NiNi}^*]}{[\text{NiNi}^*] + [\text{NiMo}^*]}, \quad (33)$$

$$p_{\text{NiMo}} = \frac{[\text{NiMo}^*]}{[\text{NiNi}^*] + [\text{NiMo}^*]} = 1 - p_{\text{NiNi}}, \quad (34)$$

$$p_{\text{MoNi}} = \frac{[\text{MoNi}^*]}{[\text{MoMo}^*] + [\text{MoNi}^*]} = 1, \quad (35)$$

$$p_{\text{MoMo}} = \frac{[\text{MoMo}^*]}{[\text{MoMo}^*] + [\text{MoNi}^*]} = 0. \quad (36)$$

The probability matrix has the form

$$P = \begin{bmatrix} p_{\text{NiNi}} & p_{\text{NiMo}} \\ 1 & 0 \end{bmatrix} \quad (37)$$

The equilibrium equations corresponding to Eqs. 30 and 31 are

$$\frac{[\text{NiNi}^*]}{[\text{Ni}^*]c_{\text{Ni}}} = K_{\text{NiNi}^*} \exp\left(-\frac{2F\Delta E}{RT}\right), \quad (38)$$

$$\frac{[\text{NiMo}^*]}{[\text{Ni}^*]c_{\text{Mo}}c_{\text{Ci}}^n} = K_{\text{NiMo}^*} \exp\left(-\frac{\Delta zF\Delta E}{RT}\right). \quad (39)$$

The following equation for the ratio of the mole fractions in the alloy is obtained

$$\frac{x_{\text{Ni}}}{x_{\text{Mo}}} = \frac{1}{p_{\text{NiMo}}} = \frac{K_{\text{NiNi}^*} \exp\left(-\frac{(2-\Delta z)F\Delta E}{RT}\right) c_{\text{Ni}} + c_{\text{Mo}}c_{\text{Ci}}^n}{c_{\text{Mo}}c_{\text{Ci}}^n}. \quad (40)$$

Introducing

$$g_{\text{Ni}} = \frac{K_{\text{NiNi}^*}}{K_{\text{NiMo}^*}} \exp\left(-\frac{(2 - \Delta z)F\Delta E}{RT}\right), \quad (41)$$

and v and w as

$$v = \frac{x_{\text{Ni}}}{x_{\text{Mo}}} \quad w = \frac{c_{\text{Ni}}}{c_{\text{Mo}}},$$

one obtains

$$v = \frac{g_{\text{Ni}} w + c_{\text{Ci}}^n}{c_{\text{Ci}}^n}. \quad (42)$$

This equation was applied to two results published by Podlaha and Landolt [4]. Experimental alloy compositions ($v = x_{\text{Ni}}/x_{\text{Mo}}$) determined for a nickel ion concentration of $c_{\text{Ni}} = 1 \text{ mol/l}$ and a concentration of MoO_4^{2-} $c_{\text{Mo}} = 0.005 \text{ mol/l}$ as a function of the current density are shown in Fig. 5. The experimental conditions correspond to $w \ll 1$ and if $g_{\text{Ni}} w \ll c_{\text{Ci}}^n$ then Eq. 42 can be approximated by

$$v \equiv \frac{x_{\text{Ni}}}{x_{\text{Mo}}} \approx 1. \quad (43)$$

Figure 5 shows that $v = x_{\text{Ni}}/x_{\text{Mo}}$ is 3 for lower current densities and is 1.5 at higher current densities. A possible explanation could be (1) $g_{\text{Ni}} w$ cannot be neglected if compared to the citrate concentration (0.7 mol/l) and (2) $g_{\text{Ni}} w$ depends on the current density, respectively, the deposition potential becoming smaller with decreasing current. Otherwise, $v = x_{\text{Ni}}/x_{\text{Mo}}$ does not depend on the convection of the electrolyte as predicted by the approximation.

The opposite case is given by a nickel ion concentration of $c_{\text{Ni}} = 0.005 \text{ mol/l}$ and a concentration of MoO_4^{2-} $c_{\text{Mo}} = 0.7 \text{ mol/l}$. The ratio $v = x_{\text{Ni}}/x_{\text{Mo}}$ as a function of the current density and for three rotation rates is shown in Fig. 6. The equation describing this situation is

$$v = \frac{g_{\text{Ni}} w}{c_{\text{Ci}}^n}. \quad (44)$$

For constant citrate concentration (0.7 mol/l) v is proportional to w . However, w depends on the current density and on the rate of rotation because the concentration of MoO_4^{2-} on the surface depends on the mass transport conditions. Similar approximations as for the CoNi system are assumed, for the dependence on current density. Additionally convection, induced by the rate of rotation of the working electrode, has to be taken into account. Increasing the rate of rotation decreases the thickness of the diffusion layer. In a rough approximation the diffusion layer is inversely proportional to the rate of rotation. Then one obtains

$$c_{\text{Mo}} = c_{0,\text{Mo}} \left(1 - k^* \frac{i}{r}\right). \quad (45)$$

The concentration ratio is

$$w \approx w_0 \left(1 + k^* \frac{i}{r}\right). \quad (46)$$

One obtains

$$v \approx \frac{g_{\text{Ni}} w_0}{c_{\text{Ci}}^n} \left(1 + k^* \frac{i}{r}\right). \quad (47)$$

Figure 6 shows $v = x_{\text{Ni}}/x_{\text{Mo}}$ is proportional to i and is inverse proportional to the rotation speed r . The dependence on the rotation speed r is also shown in Fig. 7.

The linear plots of v on i in Fig. 6 should have the same intersection point with the v -axis. The real values lead to an average intersection point of $v = g_{\text{Ni}} w_0 / c_{\text{Ci}}^n \approx 10$. With $w_0 = c_{\text{Ni}}/c_{\text{Mo}} = 0.007$ and $c_{\text{Ci}}^n = 0.7 \text{ mol dm}^{-3}$ (assuming $n = 1$) a value of $g_{\text{Ni}} \approx 1000$ is calculated, a measure of the selectivity of the alloy surface for Ni ions.

Fig. 5 Alloy composition $v = x_{\text{Ni}}/x_{\text{Mo}}$ versus potential; $c_{\text{Ni}} = 1 \text{ mol dm}^{-3}$ and $c_{\text{Mo}} = 0.005 \text{ mol dm}^{-3}$, citrate concentration 0.7 mol dm^{-3} (data taken from [4])

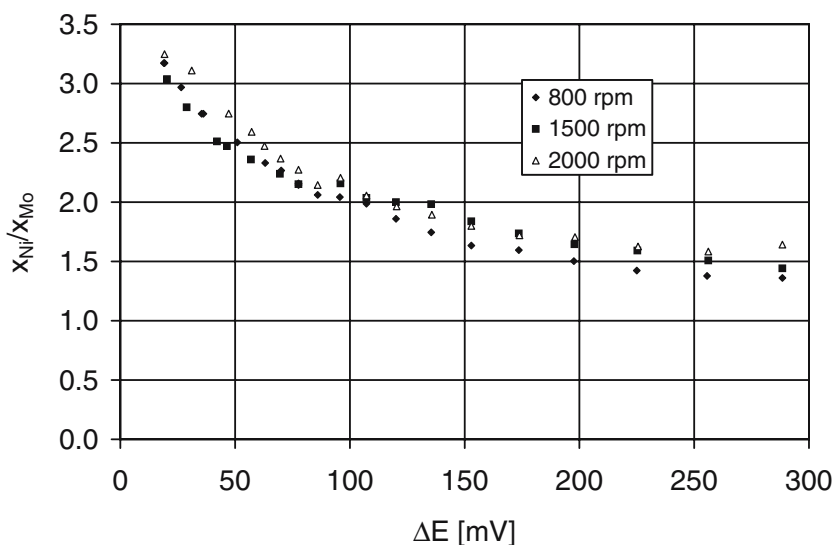


Fig. 6 Alloy composition $v = x_{Ni}/x_{Mo}$ versus current density; $c_{Ni} = 0.005 \text{ mol dm}^{-3}$ and $c_{Mo} = 0.7 \text{ mol dm}^{-3}$, citrate concentration 0.7 mol dm^{-3} (data taken from [4])

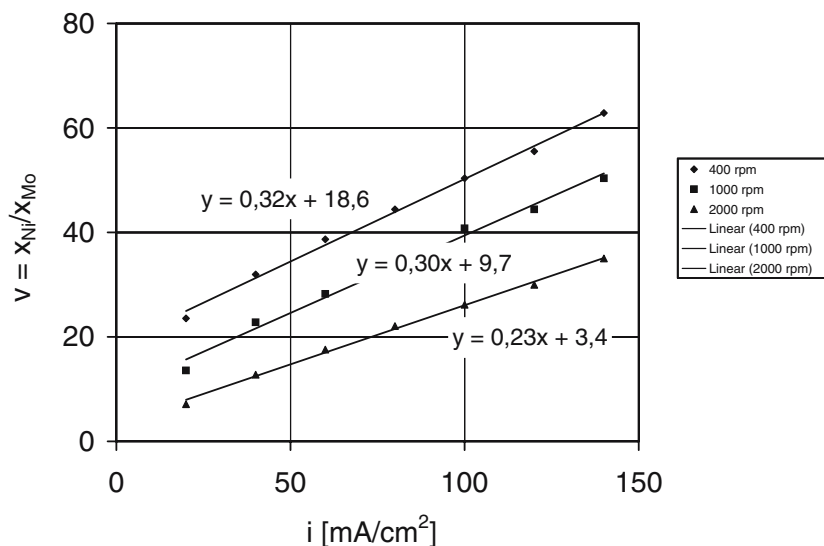
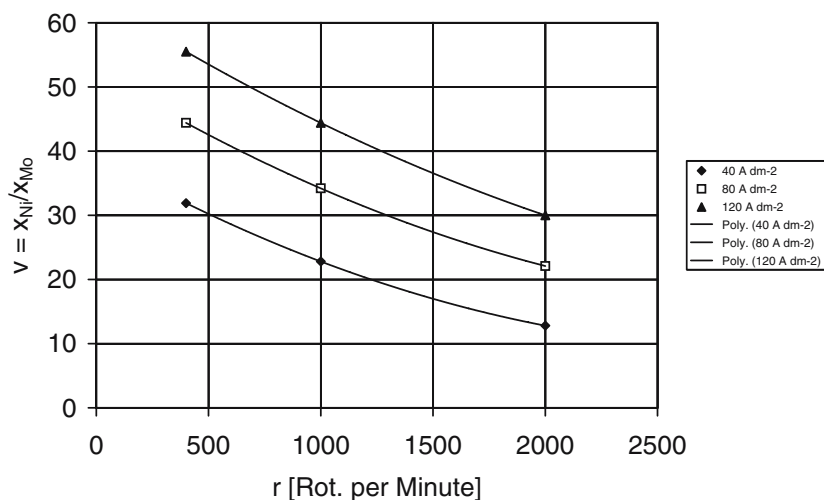


Fig. 7 Alloy composition $v = x_{Ni}/x_{Mo}$ versus rate of rotation; Ni concentration $0.005 \text{ mol dm}^{-3}$ and MoO_4^{2-} concentration 0.7 mol dm^{-3} , citrate concentration 0.7 mol dm^{-3} (data taken from [4])



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