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The effect of the concentration of the reacting ion on the control of the electrodeposition process

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Abstract: The effect of the concentration of the reacting ion on the nature of the control of the electrodeposition process was investigated by digital simulation of the polarization curve using the Newman form of the polarization curve equation and the Levich dependence of the limiting diffusion current density under natural convection conditions. A simple method for the determination of the exchange current density from polarization measurements is also proposed. The agreement with experiments was correct.

Keywords: polarization curve equation; concentration dependence.

INTRODUCTION

It was shown recently^{1,2} that instead of the general equation of the cathodic polarization curve:

$$\frac{j}{j_L} = \frac{j_0}{j_L} \left(1 - \frac{j}{j_L}\right)^\gamma (f_c - f_a) \quad (1)$$

the approximate form:

$$\frac{j}{j_L} = \frac{\frac{j_0}{j_L} (f_c - f_a)}{1 + \frac{j_0}{j_L} (f_c - f_a)} \quad (2)$$

obtained by taking $\gamma = 1$, can be used with a maximum error of 20 %. Equations (1) and (2) are modified for use in the electrodeposition of metals by taking the

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Popov *et al.*³ j , j_0 and j_L are the current density, the exchange current density and limiting diffusion current density for the cathodic process, respectively,

$$f_c = 10^{\frac{\eta}{b_c}} \quad (3)$$

and

$$f_a = 10^{-\frac{\eta}{b_a}} \quad (4)$$

and η is the overpotential, b_c and b_a are the cathodic and anodic Tafel slope, respectively, and

$$\gamma = \frac{d \log j_0}{d \log c} \quad (5)$$

where c is the concentration of the reacting ion.

It is necessary to note that Eq. (2) is an approximation because the value of γ is lower than unity.⁴ This approximation is widely used in qualitative discussions because it permits the simple mathematical treatment of electrochemical processes with relatively small errors. If $\gamma \neq 1$ is included in the derivation of the general equation of the cathodic polarization curve, simple analytical solutions are not available and numerical solutions are required.

It can be seen from Eq. (2) that the ratio j_0/j_L determines the nature of the control of the electrodeposition process. If

$$\frac{j_0}{j_L} \rightarrow 0 \quad (6)$$

the metal electrodeposition process is under activation control and if

$$\frac{j_0}{j_L} \rightarrow \infty \quad (7)$$

it is under diffusion control. On the other hand, it is known that j_0 and j_L depend on the concentration of the reacting ion. Thus, the aim of this study was to investigate the effect of the concentration of the reacting ion on the control of the electrodeposition process.

THE STATEMENT OF THE PROBLEM

It is known that the concentration dependence of the exchange current density⁴ is expressed as:

$$j_{0,c} = \left(\frac{c}{c_0} \right)^\gamma j_{0,0} \quad (8)$$

where $j_{0,c}$ and $j_{0,0}$ are the exchange current densities corresponding to the concentrations c and c_0 of the reacting ion.

The limiting diffusion current density j_L depends on the concentration of the reacting ion according to:⁵

$$j_L \approx c^n \quad (9)$$

where

$$1 \leq n \leq 1.25 \quad (10)$$

depending on the hydrodynamic conditions in the electrochemical cell. Assuming c_0 as the concentration of the reacting ion in a reference solution, it follows from Eq. (9) that:

$$j_{L,c} = \left(\frac{c}{c_0} \right)^n j_{L,0} \quad (11)$$

where $j_{L,c}$ and $j_{L,0}$ are the limiting diffusion current densities for the concentrations of the reacting ion c and c_0 , respectively, and because of Eqs. (8) and (9):

$$\frac{j_{0,c}}{j_{L,c}} = \frac{j_{0,0}}{j_{L,0}} \left(\frac{c_0}{c} \right)^{n-\gamma} \quad (12)$$

$n = 1$ is valid in the case of forced convection (stirred electrolyte). The mass and heat transfer induced by the density gradient in liquids in the gravitational field is natural or free convection. Levich⁵ gave an approximate analytical solution for estimating the diffusion flux of the component that reacts and disappears on the surface of a vertical plate in a liquid. The electrochemical deposition of metals is a fair example of this kind of reaction.

A corresponding solution can be presented in the form $j \approx c_0^{1.25}$. Several authors⁶⁻⁸ have reported a value of the concentration exponent of less than 1.25. Systematic investigations of metal electrodeposition on a vertical plate and thin metal wire^{7,8} showed that the Levich solution is valid only when the temperatures of the thermo-isolated solution and of the surrounding air are equal, *i.e.*, under proper isothermal conditions. For even a small temperature difference, the value of the concentration exponent decreases considerably (for a temperature difference of 1.5 °C, the value of the exponent is 1.08). In addition, evaporation of the solution into dry air of the same temperature flowing over the electrolyte surface can also cause a decrease of the value of the concentration exponent.

A similar effect exist in the case of a superimposed magnetic field.⁹

In the case of copper electrodeposition⁴ $\gamma = 0.75$ and

$$0.25 \leq n - \gamma \leq 0.5 \quad (13)$$

because of Eq. (10), but

$$n - \gamma \approx 0.25 \quad (14)$$

is a more realistic value even in slightly-stirred solutions, and

$$n - \gamma \approx 0.50 \quad (15)$$

for non-stirred solutions under isothermal conditions.

In both cases

$$n - \gamma < 1 \quad (16)$$

and if

$$c_0/c \rightarrow \infty \quad (17)$$

it follows from Eqs. (12), (16) and (17) that:

$$j_{0,c}/j_{L,c} \rightarrow \infty \quad (18)$$

meaning, in accordance with Eq. (7), that the degree of diffusion control increases with decreasing concentration of the reacting ion.

It was shown recently¹⁰ that the exchange current density for a process for which the mechanism is known can be easily determined from the measured polarization curve, if the *IR* error is negligible.¹¹

If

$$j = kj_L \quad (19)$$

where $0 < k < 1$, Eqs. (1) and (2) can be rewritten in the forms:

$$j_0 = \frac{kj_L}{(1-k)^\gamma (f_{c,k} - f_{a,k})} \quad (20)$$

and

$$j_{0,app} = \frac{kj_L}{(1-k)(f_{c,k} - f_{a,k})} \quad (21)$$

respectively, where j_0 and $j_{0,app}$ are the true and approximate values of the exchange current density and $f_{c,k}$ and $f_{a,k}$ correspond to the current density from Eq. (19).

Using $c_0 = 1.0 \text{ mol dm}^{-3}$ CuSO_4 in $0.50 \text{ M H}_2\text{SO}_4$ as a reference solution and the corresponding values of $j_{L,0} = 100 \text{ mA/cm}^2$ and $j_{0,0} = 10 \text{ mA/cm}^2$, $f_c = 10^{\eta/120}$ and $f_a = 10^{-\eta/40}$ and $\gamma = 0.75$ and 1 , the polarization curves for electrodeposition from $1, 0.10$ and 0.010 M CuSO_4 in $0.50 \text{ M H}_2\text{SO}_4$ are calculated using Eqs. (1), (2), (12), (14) and (15) and presented in Figs. 1 and 2. The polarization curves presented by the full lines in Figs. 1 and 2 were calculated using Eq. (1) and $\gamma = 0.75$ and the ones presented by the dashed lines, using Eq. (2) and hence, $\gamma = 1$. It can be seen from Figs. 1 and 2 that with increasing value of the $j_{0,c}/j_{L,c}$ ratio due to the decreasing concentration of the depositing ion, the degree of diffusion control increases. The polarization curves are practically the same for $\gamma = 0.75$ and 1 up to $j/j_L = 0.3$ for each j/j_L ratio. Hence, Eq. (2) can be successfully used instead of Eq. (1) in quantitative discussions at low current densities.

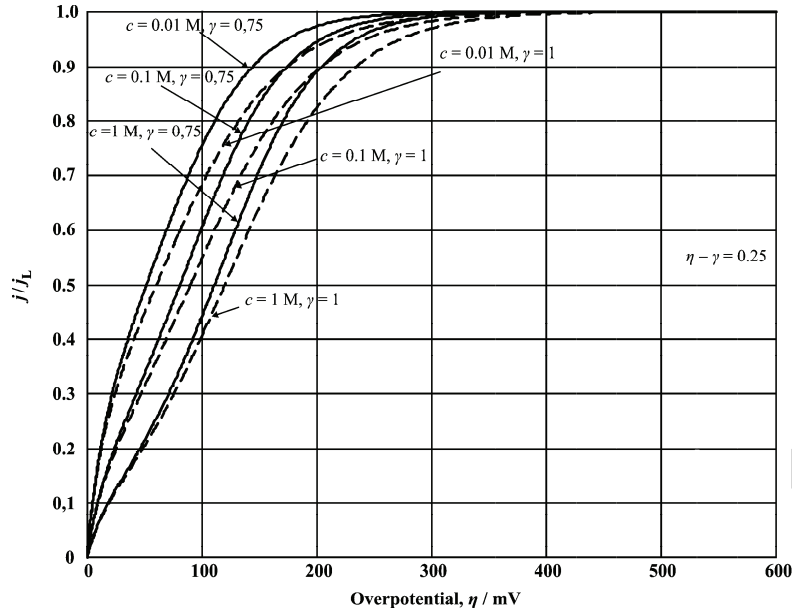


Fig. 1. Dependences $j/j_L-\eta$ calculated from Eqs. (1) and (12) using $c = 1.0, 0.10$ and 0.010 mol dm^{-3} , $c_0 = 1.0$ mol dm^{-3} , $f_c = 10^{\eta/120}$, $f_a = 10^{-\eta/40}$, $j_{L,0} = 100$ mA/cm 2 , $j_{0,0} = 10$ mA/cm 2 and $n - \gamma = 0.25$.

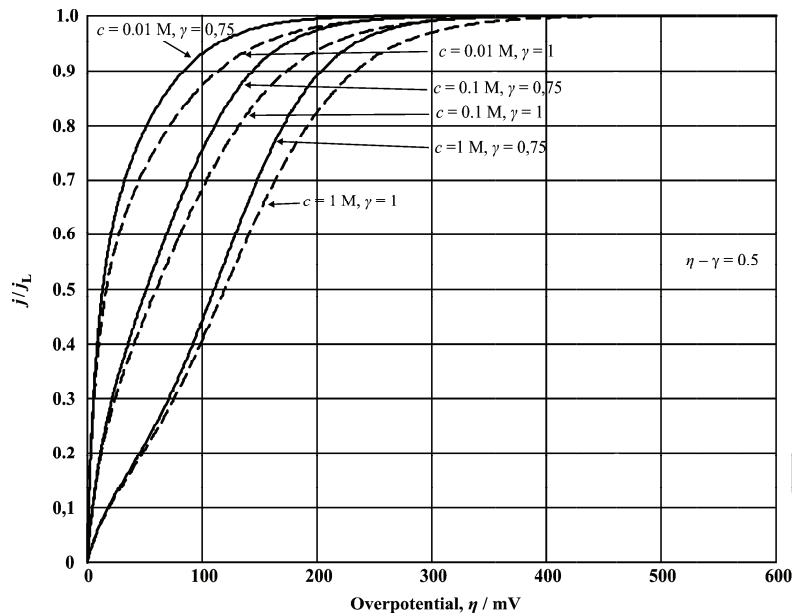


Fig. 2. Dependences $j/j_L-\eta$ calculated from Eqs. (1) and (12) using $c = 1.0, 0.10$ and 0.010 mol dm^{-3} , $c_0 = 1.0$ mol dm^{-3} , $f_c = 10^{\eta/120}$, $f_a = 10^{-\eta/40}$, $j_{L,0} = 100$ mA/cm 2 , $j_{0,0} = 10$ mA/cm 2 and $n - \gamma = 0.5$.

It follows from Eqs. (20) and (21) that

$$j_{0,\text{app}} = (1 - k)^{\gamma-1} j_0 \quad (22)$$

and the $j_{0,\text{app}}/j_0$ ratios calculated using Eq. (22) and $\gamma - 1 = 0.25$ as a function of k are presented in Table I.

TABLE I. Comparison of j_0 calculated using Eq. (8) (true values) and ones calculated using Eq. (21) (approximate values)

k	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90
$j_{0,\text{app}}/j_0$	1.03	1.06	1.09	1.14	1.19	1.26	1.35	1.50	1.78

It can be seen from Table I that Eq. (21) can be successfully employed for the determination of the value of the exchange current density from the polarization curve up to $k = 0.2$ with an error lower than 5 % and up to $k = 0.3$ with an error lower than 10 %.

Obviously, the ratio of the exchange current density to the limiting diffusion one can also be calculated in the same manner with the same error.

EXPERIMENTAL

Copper was potentiostatically deposited from the following solutions: a) 0.020 M CuSO₄ + 0.50 M H₂SO₄, b) 0.050 M CuSO₄ + 0.50 M H₂SO₄ and c) 0.10 M CuSO₄ + 0.50 M H₂SO₄.

Electrodepositions were performed in an open cell at a temperature of 23.0±0.5 °C using a Wenking 7103 GIRH potentiostat. Doubly distilled water and analytical grade chemicals were used for the preparation of solutions for the electrodeposition of copper.

The working electrode was a stationary Pt wire covered with Cu film electrodeposited at an overpotential of 300 mV during 3.0 min from 0.10 M CuSO₄ in 0.50 M H₂SO₄.

The counter electrode was a copper foil placed close to the walls of the cell; the working electrode was placed in the middle of the cell, while the overpotential was adjusted vs. a copper electrode which was positioned at a distance of 0.2 cm from the surface of the working electrode.

In order to determine the exchange current densities of electrochemically deposited copper, the electrode was prepared by electrochemical deposition of copper on a Pt wire ($S = 0.45 \text{ cm}^2$) from an aqueous solution of 0.10 M CuSO₄ in 0.50 M H₂SO₄ galvanostatically, at a constant current density of 4.0 mA/cm² during 1200 s. Then the cathodic and anodic polarization curves were recorded potentiodynamically at a scan rate of 1.0 mV s⁻¹ in solutions containing 0.020, 0.050 and 0.10 M CuSO₄ in 0.50 M H₂SO₄ in the overpotential range -120 to 100 mV. In order to reach the steady state condition, the working electrode was held at a constant cathodic overpotential of -120 mV for 120 s before the measurements. Since the cathodic polarization curves were attained under mixed control, the exchange current densities were determined from the intercept of anodic and theoretical cathodic Tafel slopes.

The experiments for determining the exchange current densities were performed in a standard three compartment electrochemical cell at ambient temperature. A copper wire (99.999 %) in the same solution was used as the reference electrode, while a platinum wire served as the counter electrode. Both galvanostatic and potentiodynamic experiments were performed using a PAR 263A potentiostat/galvanostat.

RESULTS AND DISCUSSION

The polarization curves for the electrodeposition of copper from 0.020, 0.050 and 0.10 M CuSO_4 in 0.50 M H_2SO_4 at a temperature of 23 ± 1 °C are shown in Fig. 3 and the ones normalized to the value of the limiting diffusion current density in Fig. 4.

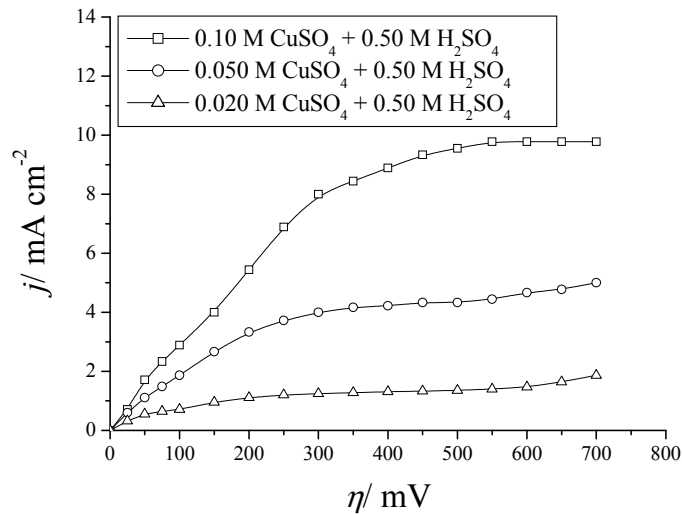


Fig. 3. Polarization curves for the electrodeposition of copper from 0.020, 0.050 and 0.10 M CuSO_4 in 0.50 M H_2SO_4 at a temperature of 23 ± 1 °C.

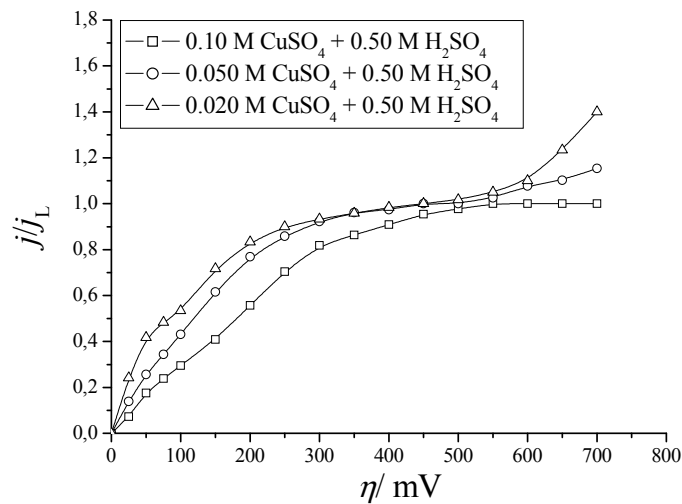


Fig. 4. Polarization curves for the electrodeposition of copper from 0.020, 0.050 and 0.10 M CuSO_4 in 0.50 M H_2SO_4 at a temperature of 23 ± 1 °C normalized to the value of corresponding limiting diffusion current density.

The fact that the value of the ratio j_0/j_L increased with decreasing concentration of Cu(II) ions can be considered a good qualitative illustration of the increasing degree of diffusion control of the deposition process with decreasing concentration of the depositing ion (Figs. 1, 2 and 4).

Assuming that the IR error can be neglected in electrodeposition from the used electrolyte solutions, the values of j_0 listed in Table II were obtained using Eq. (21) and $k = 0.30$ and the data from Fig. 3, which are in fair agreement with the values obtained by the potentiodynamic recording of cathodic and anodic polarization curves.

TABLE II. Comparison of the j_0 values estimated by the proposed method (approximate values) and those determined by the potentiodynamic recording of the cathodic and anodic polarization curves (experimental values)

c (CuSO ₄) / mol dm ⁻³ (in 0.50 M H ₂ SO ₄)	$j_{0,app}$ / mA cm ⁻²	$j_{0,exp}$ / mA cm ⁻²
0.020	0.36	0.24
0.050	0.54	0.70
0.10	0.85	1.3

Simultaneously, a simple method for the estimation of exchange current densities from polarization measurements is demonstrated.

In this way, it was shown that the degree of diffusion control increases with decreasing concentration of the reacting ion in metal electrodeposition processes, as was estimated earlier from the morphology of electrodeposited metals.¹²

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ИЗВОД

УТИЦАЈ КОНЦЕНТРАЦИЈЕ РЕАГУЈУЋЕГ ЈОНА НА КОНТРОЛУ ПРОЦЕСА ЕЛЕКТРОХЕМИЈСКОГ ТАЛОЖЕЊА

ПРЕДРАГ М. ЖИВКОВИЋ¹, НЕБОЈША Д. НИКОЛИЋ², МИЛИЦА ГВОЗДЕНОВИЋ¹ И КОНСТАНТИН И. ПОПОВ^{1,2}

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У раду је испитиван утицај концентрације реагујућег јона на врсту контроле процеса електрохемијског таложења. Примењена је дигитална симулација поларизационих кривих на основу Newman-овог облика једначине поларизационе криве и Levich-еве зависности граничне дифузионе густине струје у условима природне конвекције. Предложен је једноставан метод одређивања густине струје измене на основу поларизационих мерења. Добијена је задовољавајућа сагласност са експериментално добијеним вредностима.

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