Journal of the Serbian Chemical Society
JSCS@tmf.bg.ac.yu • www.shd.org.yu/JSCS
*J. Serb. Chem. Soc.* 73 (2) 227–231 (2008) UDC 535.513+512.77+517968.2:541.138–034:681.5.017
*JSCS–3705* *Note*

NOTE

# The validity of the general polarization curve equation approximation for the process of metal deposition

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(Received 15 June, revised 28 September 2007)

*Abstract*: Digital simulation was employed for the solution of the general polarization curve equation of metal deposition processes. By approximating the dependence of the exchange current density on concentration with a linear function for one- and two-electron transfer processes, an error lower than 20 % was obtained.

*Keywords*: polarization curve equation; metal deposition; exchange current density; simulation.

## INTRODUCTION

The general equation of the polarization curve for metal deposition process according to Newman,[1] can be given as:

$$j = j_{0,s}\,(f_a - f_c) \tag{1}$$

where $j$ is the overall current density, $f_a$ and $f_c$ are defined as:

$$f_a = 10^{\frac{\eta}{b_a}} \tag{2a}$$

$$f_c = 10^{-\frac{\eta}{b_c}} \tag{2b}$$

where $b_a$ and $b_c$ are the anodic and cathodic Tafel slopes, respectively, $\eta$ is the overpotential and $j_{0,s}$ is the concentration dependent exchange current density for a surface concentration $c_s$. The mathematical expression for the $j_{0,s}$ could be given as:[1]

$$j_{0,s} = \left(\frac{c_s}{c_0}\right)^{\gamma} j_0 \tag{3}$$

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doi: 10.2298/JSC0802227Z

where $c_s$ and $c_0$ are the surface and bulk concentration of the reacting metal ion, respectively, $j_0$ is the exchange current density for a surface concentration equal to the bulk concentration of the solution and the coefficient $\gamma$ is defined as:

$$\gamma = \frac{\mathrm{d}\log j_0}{\mathrm{d}c_0} \tag{4}$$

For a one-electron process of metal deposition:[2]

$$Me^+ + e^- = Me \tag{5}$$

$\gamma$ is defined as:

$$\gamma = 1 - \beta \tag{6}$$

where $\beta$ is a symmetry factor of the energetic barriers.

For a two-electron process,[1] assuming the first electron transfer is rate determining in the overall mechanism:

$$Me^{2+} + e^- = Me^+ \text{ (slow)} \tag{7}$$

$$Me^+ + e^- = Me \text{ (fast)} \tag{7a}$$

$\gamma$ is defined as:

$$\gamma = \frac{2 - \beta}{2} \tag{8}$$

If $\gamma$ is not equal to 1, simple analytical solutions of the general equation of the polarization curve in terms of formal kinetics are not available and different numerical methods must be applied.

The aim of this work was to deduce whether the approximation of the value of $\gamma$ equal to 1 could be applied for the solution of the general equation of the polarization curve in a qualitative or quantitative manner.

## RESULTS AND DISCUSSION

For one-electron transfer processes given by Eq. (5), it can be calculated that the anodic and cathodic Tafel slopes have values of 120 mV/dec, while for two-electron transfer processes given by Eqs. (7) and (7a), the anodic and cathodic Tafel slopes have values of 40 and –120 mV/dec, respectively.

On the other hand, surface and bulk concentration of the reacting metal ion can be connected with current density using the following equation:

$$\frac{c_s}{c_0} = 1 - \frac{j}{j_L} \tag{9}$$

where $j_L$ is the limiting diffusion current density (note: Eq. (9) is strictly valid only in the case of forced convection, *i.e.*, a stirred electrolyte, but many authors use this equation for non-stirred conditions). By substituting $c_s/c_0$ from Eq. (9) into Eq. (3) and $j_{0,s}$ from Eq. (3) into Eq. (1), the following is obtained:

$$j = j_0\left(1-\frac{j}{j_L}\right)^{\gamma}(f_a - f_c) \tag{10}$$

or:

$$\frac{j}{j_L} = \frac{j_0}{j_L}\left(1-\frac{j}{j_L}\right)^{\gamma}(f_a - f_c) \tag{11}$$

as the general polarization curve equation.

In the first approximation, assuming the value for $\gamma \approx 1$, and with further rearrangement, a simplified version of Eq. (10) is obtained:

$$j = \frac{j_0(f_a - f_c)}{1+\frac{j_0(f_a - f_c)}{j_L}} \tag{12}$$

or:

$$\frac{j}{j_L} = \frac{\frac{j_0}{j_L}(f_a - f_c)}{1+\frac{j_0(f_a - f_c)}{j_L}} \tag{13}$$

Simplified mathematical treatments of Eqs. (12) and (13) are widely used in qualitative, and in many cases in quantitative, discussions of metal deposition and other electrochemical processes. It is again necessary to note that both equations are approximations because the value of $\gamma$ is not unity in many cases. Different numerical methods should be applied in these cases, as suggested previously.[3]

Hence, in this work, digital simulation was performed for one- and two-electron transfer processes and $\beta = 0.5$. Obviously, for a one-electron transfer process, the values are as following: $\gamma = 0.5$, $f_a = 10^{\eta/120}$ and $f_c = 10^{-\eta/120}$, while for a two-electron transfer process $\gamma = 0.75$, $f_a = 10^{\eta/40}$ and $f_c = 10^{-\eta/120}$.

The polarization curves calculated using Eqs. (11) and (13) for the ratio between $|j_0/j_L| = 10$, 1 and 0.1 are shown in Figs. 1 and 2.

As can be seen from Figs. 1 and 2, the approximation of Eq. (11) by Eq. (13) is acceptable for qualitative purposes at practically all overpotentials and ratios of $|j_0/j_L|$. On the other hand, quantitative approximation is valid only in the overpotential region where the Tafel approximation could be applied.

The relative error, given as the percentage difference of the current density between Eqs. (11) and (13), is plotted as a function of the overpotential in Figs. 3 and 4.

From Figs. 3 and 4, it can be seen that the maximum difference between the values of current density calculated using Eqs. (11) and (13) is about 20 % if $\gamma$ is 0.5 and about 9 % if $\gamma$ is 0.75.

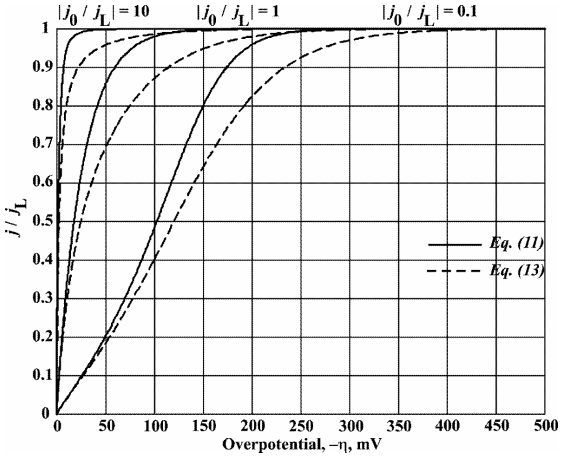


Fig. 1. Dependences of $j/j_L$ *vs.* $-\eta$ calculated from Eq. (11) and Eq. (13), using $|j_0/j_L| = 10$, 1 and 0.1, and $\gamma = 1$ and 0.5, $f_a = 10^{\eta/120}$ and $f_c = 10^{-\eta/120}$.

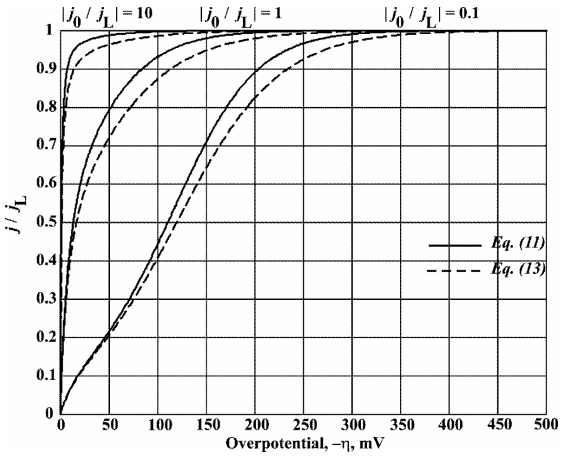


Fig. 2. Dependences of $j/j_L$ *vs.* $-\eta$ calculated from Eq. (11) and Eq. (13), using $|j_0/j_L| = 10$, 1 and 0.1, and $\gamma = 1$ and 0.75, $f_a = 10^{\eta/40}$ and $f_c = 10^{-\eta/120}$.

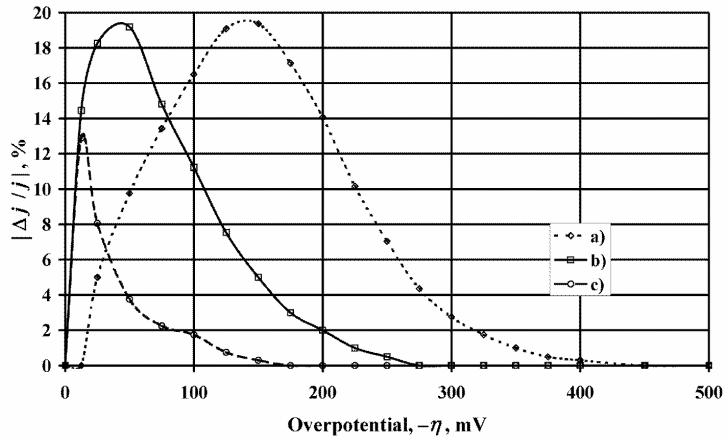


Fig. 3. Dependence $|\Delta j/j|$ *vs.* $(-\eta)$ from Fig. 1, for different $|j_0/j_L|$ ratios: a) 0.1, b) 1 and c) 10.

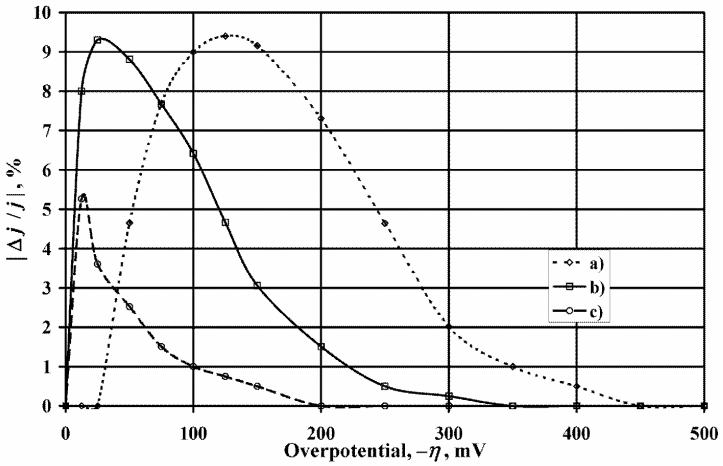


Fig. 4. Dependence $|\Delta j/j|$ *vs.* $(-\eta)$ from Fig. 2, for different $|j_0/j_L|$ ratios: a) 0.1, b) 1 and c) 10.

Hence, it can be concluded that approximation of the general polarization curve for the case of $\gamma = 1$ can be used in all qualitative and some quantitative estimations with a maximum error lower than 20 % for the cases under consideration.

*Acknowledgements*. This work was financially supported by the Ministry of Science of the Republic of Serbia, contract No. 142044.

И З В О Д

## ВАЛИДНОСТ ЈЕДНАЧИНЕ АПРОКСИМАЦИЈЕ ОПШТЕ ПОЛАРИЗАЦИОНЕ КРИВЕ ЗА ТАЛОЖЕЊЕ МЕТАЛА

ПРЕДРАГ. М. ЖИВКОВИЋ, БРАНИМИР. Н. ГРГУР И КОНСТАНТИН. И. ПОПОВ

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За решавање једначине опште поларизационе криве за процес таложења метала примењена је дигитална симулација. Апроксимирајући зависност густине струје измене од концентрације линеарном функцијом, за процесе са једноелектронским и двоелектронским трансфером добијена је релативна грешка која не прелази 20 %.

(Примљено 15. јуна, ревидирано 28. септембра 2007)

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