

Bi electrodeposition on Pt in acidic medium

2. Hydrodynamic voltammetry

Ignas Valsiūnas*,

Laima Gudavičiūtė,

Vidmantas Kapočius and

Antanas Steponavičius

*Institute of Chemistry,
A. Goštauto 9,
LT-01108 Vilnius, Lithuania*

A Pt rotating disc was used to provide some kinetic information concerning the electrodeposition of bismuth from Bi^{3+} acidic perchlorate solution 1 M HClO_4 + 0.05 M $\text{Bi}(\text{ClO}_4)_3$ at 20 °C. The electrodeposition of Bi from this solution may be interpreted in terms of an irreversible stepwise discharge of Bi^{3+} ions proceeding either through three successive one-electron steps with the transfer of the first electron as the rate-limiting step or via two successive steps with the transfer of two electrons in the first stage as the rate-limiting step. From the experimental data the diffusion coefficient D for Bi^{3+} ion was calculated and was found to be $4.9 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

Key words: bismuth, electrodeposition, perchlorate solutions, Pt rotating disc electrode, rate-determining steps

INTRODUCTION

Although bismuth, as a semimetal, exhibits some unusual thermal, electrical and magnetic properties that make its actual and potential applications [1, 2] to be rather wide, its electrochemical reduction from Bi^{3+} solutions has not been studied very extensively. Several electrochemical studies have been devoted to the investigation of current-potential (i/E) characteristics [3–7]. In most investigations of Bi deposition only electrolysis in an unstirred Bi^{3+} solution under a potential control has been employed, and these cannot give sufficient information on the kinetics and mechanism of the process. Such statement can be supported by the results of our recent work [7] in which we have shown that the experimental relationships between the characteristics of cyclic voltammograms (CVs) and the conditions of electrolysis, including the Bi^{3+} concentration (c), potential sweep rate (v) and the number of cycles (n) during a successive cycling do not completely satisfy the diagnostic criteria for a reversible or a totally irreversible electrochemical reaction predicted by the cyclic voltammetry (CV) theory [8, 9]. On the basis of these results, it has been suggested [7] that charge transfer during the Bi deposition onto a Pt electrode should be a more complex process consisting of several separate steps.

To the best of our knowledge, there is only one work [10] in which the voltammetric data, under hydrodynamically-defined conditions, have been reported for the electrodeposition of Bi.

In the present study, which is a continuation of our previous work [7], a rotating disc electrode (RDE)

technique was therefore employed in order to elucidate the further information on the mechanism of Bi electrochemical deposition on a polycrystalline Pt (Pt(poly)) electrode.

EXPERIMENTAL

Details on the preparation of perchlorate Bi^{3+} solution, on the electrochemical cell, instrumentation and the preparation of a Pt RDE (1 cm^2 in area) have been reported previously [7]. The working solution containing 0.05 M $\text{Bi}(\text{ClO}_4)_3$ + 1 M HClO_4 was used for electrochemical measurements. The potential of Pt RDE (E) was scanned slowly (5 mV s^{-1}) during rotation. All potentials in the paper are quoted versus the standard hydrogen electrode (SHE).

THEORETICAL ANALYSIS

For a bare rotating disc electrode, the current measured under non-limiting conditions is related to the kinetic and diffusion-controlled currents by the Levich–Koutecky (K–L) equation [11]:

$$1/i = 1/i_{\text{kin}} + 1/Bw^{1/2}, \quad (1)$$

where i_{kin} is the kinetically controlled current in the absence of the mass transfer effects and B is the inverse of the K–L slope at each potential. In the diffusion-controlled region, the limiting current i_{lim} is described by the following Levich (L) equation [11]:

$$i_{\text{lim}} = 0.62nFAD^{2/3}cv^{-1/6}w^{1/2}, \quad (2)$$

where n , D , A , n , c and w are the number of the exchanged electrons, diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$),

* Corresponding author. E-mail: ignas@ktl.mii.lt

apparent area of RDE (cm^2), kinematic viscosity ($\text{cm}^2 \text{s}^{-1}$), bulk concentration of a reactant (mol cm^{-3}) and RDE rotation rate (rad s^{-1}), respectively. The kinetic current is described by the following equation [11] :

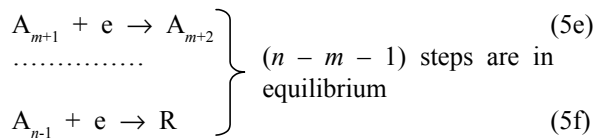
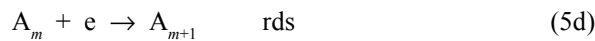
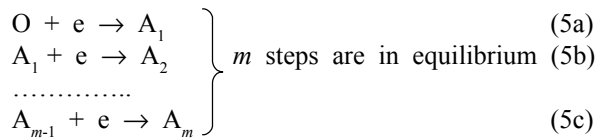
$$i_{\text{kin}} = nFAk_f c, \quad (3)$$

where k is the potential-dependent forward rate constant and the other variables are as described above.

It is generally agreed [11–13] that if more than one electron is transferred during an electrode reaction, the mechanism of such process is usually analyzed using the following simplifying assumptions: (i) only one electron is transferred in an elementary step; (ii) one of the elementary steps is much slower than the others and, therefore, is a rate-determining step (rds), the elementary processes preceding the rds are at quasi-equilibrium. Then, considering the reduction reaction involving the transfer of n electrons,



the sequence of steps can be described as follows (see, e. g. [14]):



The concentration of A_1 at the surface of the electrode (c_1) can be determined from the Nernst equation:

$$E = E_1^0 + (RT/F)\ln(c_0/c_1) \quad (6)$$

$$c_1 = K_1 c_0 \exp(-FE/RT), \quad (7)$$

where E_1^0 is the formal electrode potential of the reaction of the 1st electron transfer, the constant

$$K_1 = \exp(FE_1^0/RT).$$

Similarly,

$$c_2 = K_2 c_1 \exp(-FE/RT) = K_2 K_1 c_0 \exp(-2FE/RT) \quad (8)$$

$$c_m = K_m c_{m-1} \exp(-FE/RT) = K_f c_0 \exp(-mFE/RT), \quad (9)$$

where the constant $K_m = \exp(FE_i^0/RT)$, $i = 1, 2, \dots, m$,

and the constant $K_f = \prod_{i=1}^m K_i = \exp[(F/RT) \sum_{i=1}^m E_i^0]$.

The forward reaction current of the rds, i_{fm} , can be expressed as follows [14]:

$$\begin{aligned} i_{fm} &= FA k_{m+1}^0 c_m \exp[-(\alpha_c F/RT)(E - E_{m+1}^0)] = \\ &= FA k_{m+1}^0 (K_{m+1})^{\alpha_c} K_f c_0 \exp[-(m + \alpha_c)(FE/RT)], \end{aligned} \quad (10)$$

where k_{m+1}^0 is the standard reaction rate constant at E_{m+1}^0 of the rds, α_c is the cathodic transfer coefficient

(the symmetry factor) of the rds, A is the electrode surface area.

The overall current is

$$-i = n(i_{fm} - i_{bm}) = i_f - i_b, \quad (11)$$

where i denotes the overall reaction net current which is negative for the reduction reaction, i_{bm} is the backward reaction current of the rds, i_f and i_b represent the forward and backward reaction current of the overall reaction, respectively.

Then, following the considerations in the literature, e.g. [14], the overall current can be represented as follows:

$$-i = i_0 \{ \exp[(m + \alpha_c)(F\eta/RT)] - \exp[-(n - m - \alpha_a)(F\eta/RT)] \} = i_0 [\exp(\alpha_{c,\text{app}} F\eta/RT) - \exp(-\alpha_{a,\text{app}} F\eta/RT)], \quad (12)$$

where i_0 is the exchange current at the equilibrium potential E_{eq} , α_c and α_a are the cathodic and anodic transfer coefficients of the rds, $\alpha_{c,\text{app}} = m + \alpha_c$ and $\alpha_{a,\text{app}} = n - m - \alpha_a$ are the apparent transfer coefficients, respectively. Obviously, there is $\alpha_{c,\text{app}} + \alpha_{a,\text{app}} = n$ and $\alpha_{c,\text{app}}/\alpha_{a,\text{app}} = (m + \alpha_c)/(n - m - \alpha_a)$, while $\alpha_c + \alpha_a = 1$, which only holds if the same step remains rate-controlling over the wide range of the η involved [13]. The stoichiometric number ν^* here is assumed to be 1. In most systems α_c or α_a turns out to lie between 0.3 and 0.7, and it can be approximated to 0.5 in the absence of actual measurements.

In the case of the overall electrode reaction studied



$n = 3$, $\alpha_{c,\text{app}}/\alpha_{a,\text{app}} = (m + \alpha_c)/(3 - m - \alpha_a)$. Then, if the transfer of the 1st electron is the rds, $m = 0$, and $\alpha_{c,\text{app}}/\alpha_{a,\text{app}} = \alpha_c/(3 - \alpha_a)$. α_c is predicted to be equal to $\alpha_{c,\text{app}}$. If the transfer of the 2nd electron is the rds, then $m = 1$, $\alpha_{c,\text{app}} = 1 + \alpha_c$ and $\alpha_{a,\text{app}}/\alpha_{c,\text{app}} = (1 + \alpha_c)/(2 - \alpha_a)$. If the transfer of the 3rd electron is the rds, then $m = 2$, $\alpha_{c,\text{app}} = 2 + \alpha_c$ and $\alpha_{a,\text{app}}/\alpha_{c,\text{app}} = (2 + \alpha_c)/(1 - \alpha_a)$.

For multistep electrode reactions, in the absence of mass-transport limitations and at high overpotentials, η , particularly, at high η_c , the cathodic Tafel slope $b_c = \delta\eta_c/\delta\log|i| = 2.303RT/\alpha_{c,\text{app}}F$. Then, for the overall electrode reaction (13) and taking $\nu^* = 1$, $T = 293\text{K}$, the following experimental values of b_c can be predicted: 116, ca. 39 and ca. 23 mV dec^{-1} for the transfer of the 1st, 2nd and 3rd electron as the rds, respectively.

In general (see, e.g. [13]), most electrode processes, especially those with more than one charge transfer event, may also involve adsorption and desorption of primary reactants, intermediates and ultimate products. On the other hand, in general, for such complex electrochemical systems, there is a certain difficulty in a making distinction between the overall n value of the electrode reaction (4) and the number of electrons of the rds, usually designed as z because the latter may not be readily apparent.

A multielectron electrode reaction may also occur via a number of routes including sequential and parallel pathways that in complex kinetics can also be analyzed individually in terms of elementary electrochemical or chemical steps. It is quite obvious that at the given E in sequential reactions, the step with the smaller rate coefficient k_f is the rds, whereas in parallel paths the observed i will be determined by the path with a larger value of k_f [12, 13].

RESULTS AND DISCUSSION

RDE experiments were performed to obtain the kinetic information on the process of the discharge of Bi^{3+} ion. This process on the Pt RDE is characterized by a sole wave (Fig. 1). It was found that the determination of the i_{lim} presented no difficulty up to ca. 1200 rpm or 127 rad s^{-1} . At higher w values of the Pt RDE used here, the experimental determination of i_{lim} becomes more difficult because i_{lim} is no longer well defined.

In the experiments, the currents were analyzed both in the limiting conditions using a Levich plot i_{lim} vs. $w^{1/2}$ and in the non-limiting conditions applying a plot i vs. $w^{1/2}$ and also a Levich–Koutecky plot i^{-1} vs. $w^{-1/2}$.

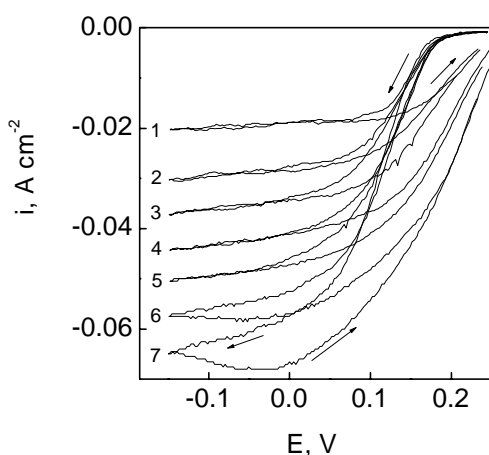


Fig. 1. Cathodic current vs. potential curves at different Pt RDE rotation speed (w) in $0.05 \text{ M Bi}(\text{ClO}_4)_3 + 1 \text{ M HClO}_4$ solution. w : 1 – 14.1, 2 – 25.1, 3 – 39.3, 4 – 56.5, 5 – 76.9, 6 – 100.5 and 7 – 127.2 rad s^{-1} . Potential sweep rate 5 mV s^{-1}

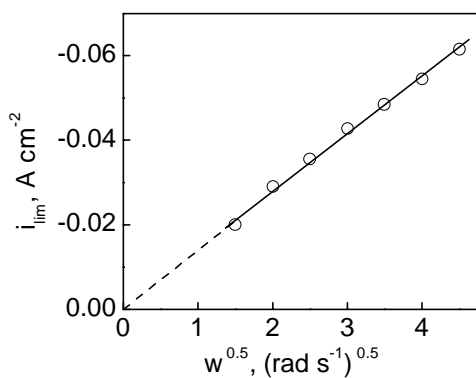


Fig. 2. Levich limiting current vs. square root of rotation speed plot obtained from the data in Fig. 1

The limiting currents for the Bi deposition plotted against $w^{1/2}$ are shown in Fig. 2. i_{lim} depends linearly on $w^{1/2}$ and shows a zero intercept indicating the limiting diffusion control, as predicted by the L Eq. (2). From the experimental slope $\delta i_{\text{lim}}/\delta w^{1/2}$ for $n = 3$, $\nu = 0.01 \text{ cm}^2 \text{ s}^{-1}$ and $c = 5 \cdot 10^{-5} \text{ mol cm}^{-3}$, the diffusion coefficient D for Bi^{3+} ion was found to be $4.9 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. It can be noted that this magnitude of D is in reasonable agreement with $D = 5.7 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ measured earlier with the Pt RDE in the Bi^{3+} perchlorate solution [10], but it differs more significantly from the value of $(8 \pm 1) \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ obtained from the chronoamperometric data in the solution $0.05 \text{ M Bi}(\text{NO}_3)_3 + 5.8 \text{ M HNO}_3$ [5].

Further, the currents recorded with the Pt RDE for the non-limiting conditions, in particular for the potential on the ascending portion of the voltammogram in the range $+0.130$ to $+0.080 \text{ V}$, were used to construct the plot i vs. $w^{1/2}$. As one can see from Fig. 3, in all cases for this E window, i practically linearly depends on $w^{1/2}$ with non-zero intercepts. Therefore, it can be suggested that although rather clear indications of the presence of a mixed control under the conditions of the Bi electrodeposition are revealed, the diffusion-controlled component is still of first importance in the experimentally registered total i .

Applying the K–L equation (1) for the determination of the kinetically controlled current i_{kin} , the straight lines i^{-1} vs. $w^{-1/2}$ were obtained in the E_{kin} range $+0.13$ to $+0.08 \text{ V}$ (Fig. 4). The slope of these plots, $\delta i^{-1}/\delta w^{-1/2}$, was found to depend slightly on E . In the meantime, we cannot clearly explain the reasons for such a deviation from the parallelism mentioned above. Formally speaking, such a circumstance might be considered as a certain indication that the reaction order in respect of the bulk c of Bi^{3+} somewhat differs from the first reaction order. On the other hand, it should be noted that this feature of the plots i^{-1} vs. $w^{-1/2}$ can arise not only from a variation in the reaction order, but also from other reasons. In order to elucidate the reason for this feature, some additional experiments are needed.

The experimental values of the parameter B derived from the data presented in Fig. 4 are $5.23 \cdot 10^{-3}$ to $6.31 \cdot 10^{-3} \text{ A cm}^{-2} \text{ s}^{1/2}$ which compare favourably with the value of $6.34 \cdot 10^{-3} \text{ A cm}^{-2} \text{ s}^{1/2}$, calculated using the Schmidt number corrected Newman's expression for B [15]:

$$B = nF\nu^{1/2}c\{0.621(\nu/D)^{-2/3}[1 + 0.298(\nu/D)^{-1/3} + 0.145(\nu/D)^{-2/3}]\} \quad (14)$$

with $c = 5 \cdot 10^{-5} \text{ mol cm}^{-3}$, $\nu = 0.01 \text{ cm}^2 \text{ s}^{-1}$, $D = 5.7 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ [10] and $n = 3$.

From the intersections of the K–L plots (Fig. 4), the values of i_{kin} were determined and used to construct the mass-transport corrected Tafel plot for the case of the discharge of Bi^{3+} at the Pt RDE (Fig. 5). The slope of this plot was obtained to be $b_{c,1} = 62 \text{ mV dec}^{-1}$ for the E range $+130$ to $+80 \text{ mV}$.

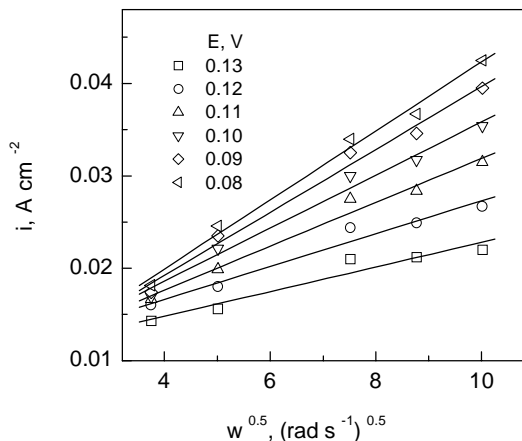


Fig. 3. Current vs. square root of rotation speed plots obtained from the data in Fig. 1 at various E

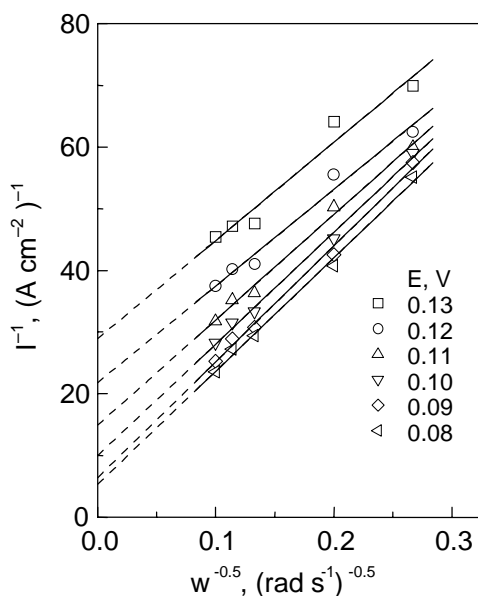


Fig. 4. Koutecky-Levich plots i^{-1} vs. $w^{-1/2}$ obtained from the data in Fig. 1 at various E

According to Cheh and Sard [16], another form of the Volmer–Tafel equation, when the anodic portion of the equation is neglected is:

$$E = [-RT/(1 - \alpha_c nF)] \ln[i/i_0(1 - i/i_{lim})] + E^0, \quad (15)$$

where E^0 is the equilibrium potential. A corresponding plot of the $\log[i \cdot i_{lim}/(i_{lim} - i)]$ vs. E at various w is presented in Fig. 6. The slope of the approximating straight line was found to be $b_{c,2} \approx 80 \text{ mV dec}^{-1}$.

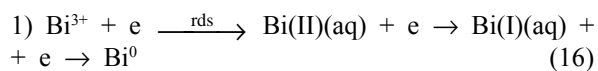
It is unclear what leads to this difference between the experimental values of the Tafel slope $b_{c,1}$ and $b_{c,2}$. Whether or not the overall electrode reaction (13) proceeds through the one-electron steps and which step is the rds is still to be elucidated because both values of the Tafel slope differ from those obtained with $\alpha_c = 0.5$ and $z = 1$ and sometimes quoted as “typical” Tafel slopes [17].

According to theoretical analysis, the experimental value of $b_{c,2}$, ca. 80 mV dec^{-1} , may be expected only in the

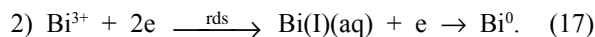
case where the overall reaction (13) occurs in three successive one-electron steps with the transfer of the first electron as the rds and with $\alpha_c = 0.72$. The other magnitude of the cathodic Tafel slope, $b_{c,1} = 62 \text{ mV dec}^{-1}$, is not the one that is normally expected for this mechanism.

On the other hand, if one assumes the rate constants k_f of the transfer of the first and the second electrons to be close, i.e., the overall electrode reaction (13) is assumed to proceed in two steps, the first step involving two-electron transfer as the rds, and the second step with one-electron transfer, both of the experimental values of b_c mentioned above can be applied in the calculation of the kinetic parameters $\alpha_c z$ and a_c . In the same E region, $b_{c,1}$ and $b_{c,2}$ give $\alpha_c z = 0.94$, $\alpha_c = 0.47$ and $\alpha_c z = 0.72$, $\alpha_c = 0.36$, respectively.

Using the experimental facts concerning the electrode process under study, the following mechanisms can formally be suggested:



or



Considering the nature of the Bi species in perchlorate solutions, it should be noted that in strongly acidic media (in our case, 1 M HClO_4) the aqua Bi^{3+} prevails (>97%) and that hydrolyzed forms such as $\text{Bi}_6(\text{OH})_{12}^{6+}$

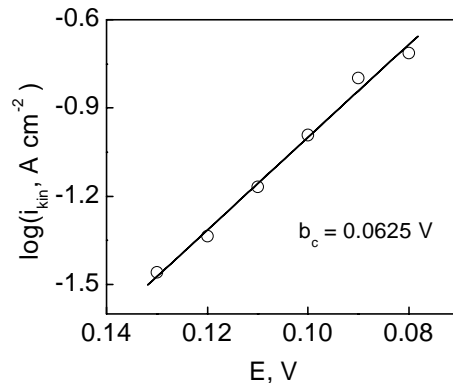


Fig. 5. Cathodic Tafel plot obtained from the data in Fig. 4

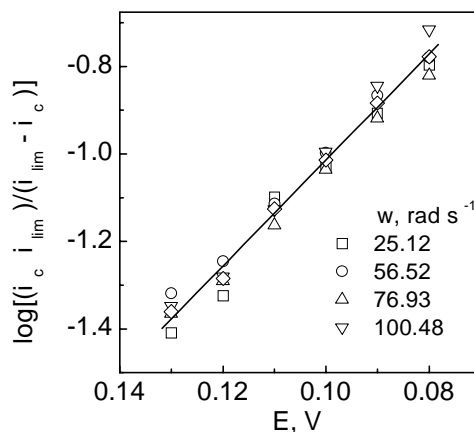


Fig. 6. Plot of $\log[i \cdot i_{lim}/(i_{lim} - i)]$ vs. E constructed according to the equation (15)

and BiOH^{2+} exist only to a very small extent [18]. As far as we know, the literature data on the chemistry of Bi intermediates such as Bi(II)(aq) and Bi(I)(aq) appear to be rather scarce, especially the data related to the Bi(II) species. The presence of the Bi(I) species has been noted in some earlier works (see, e.g. [2, 19, 20]). It is noteworthy that the electrode reaction of Bi^{3+} reduction to Bi^+ and finally from Bi^+ to Bi, has been considered when the deposition of Bi from an aqueous nitrate solution onto different substrates was studied using the cyclic voltammetry, XRD and SEM techniques [2].

In any case, presently it seems to be rather complicated to discriminate between these two suggested mechanisms of Bi deposition onto Pt from an acidic perchlorate solution. The first mechanism is commonly accepted to be sufficiently suitable for most multielectron systems because of its rather detailed theoretical background (see, e.g. [12–14]). Analogous mechanism has already been proposed for some systems, for instance, for the As deposition on Au(111) substrate in a phosphate buffer [14]. The second mechanism involves a stage of the transfer of two electrons simultaneously, as the rds. Such mechanism is considered more rarely at present [12, 13].

CONCLUSIONS

The electrodeposition process of bismuth onto polycrystalline Pt rotating disc electrode from 1 M HClO_4 + 0.05 M $\text{Bi}(\text{ClO}_4)_3$ solution at 20°C was found to be an irreversible electrode reaction. On the basis of the analysis of the Tafel plots constructed using the Pt RDE data, two possible reaction mechanisms were proposed. According to the first mechanism, the electrode reaction proceeds through three continuous one-electron steps with the transfer of the first electron as the rate-determining step, and other two steps are in equilibrium. The second mechanism involves a simultaneous transfer of the first and the second electrons as the rds. It is rather problematic to decide which of these proposed mechanisms is more suitable. The value of the diffusion coefficient for Bi^{3+} ion calculated from the dependence of the cathodic limiting current on the rotation speed of RDE was found to be $4.9 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

Received 20 June 2006

Accepted 07 July 2006

References

1. K. Liu, C. L. Chien, P. C. Searson and K. Yu-Zhang, *Appl. Physics Letters*, **73**, 1436 (1998).
2. Sh. Jiang, Y.-H. Huang, F. Luo, N. Du and Ch.-H. Yan, *Inorg. Chem. Commun.*, **6**, 781 (2003).
3. M. Takahashi, Y. Oda, T. Ogino and Sh. Furuta, *J. Electrochem. Soc.*, **140**, 2550 (1993).
4. J. P. Ziegler, *Solar Energy Materials & Solar Cells*, **56**, 477 (1999).
5. C. O'Reilly, G. Hinds and J. M. D. Coey, *J. Electrochem. Soc.*, **148**, C674 (2001).
6. M. S. Martín-González, A. L. Prieto, R. Gronsky, T. Sands and A. M. Stacy, *J. Electrochem. Soc.*, **149**, C546 (2002).
7. I. Valsiūnas, L. Gudavičiūtė and A. Steponavičius, *Chemija*, **16** (3-4), 21 (2005).
8. R. S. Nicholson and I. Shain, *Analyt. Chem.*, **36**, 706 (1964).
9. R. Greef, R. Peat, L. M. Peter, D. Pletcher and J. Robinson, *Instrumental Methods in Electrochemistry*, Chapt. 6, John Wiley & Sons, New York–Chichester–Brisbane–Toronto (1985).
10. S. H. Cadle and St. Bruckenstein, *Analyt. Chem.*, **44**, 1993 (1972).
11. A. J. Bard and L. R. Faulkner, *Electrochemical Methods. Fundamentals and Applications*, Chapt. 8, John Wiley & Sons, New York–Chichester–Brisbane–Toronto–Singapore (1980).
12. I. Rubinstein, *Physical Electrochemistry* (Ed. I. Rubinstein), Chapt. 1, Marcel Dekker Inc., New York–Basel–Hong Kong (1995).
13. E. J. Calvo, *Comprehensive Chemical Kinetics* (Eds. C. H. Bamford and R. G. Compton), Vol. 26, *Electrode Kinetics. Principles and Methodology*, Chapt. 1, Elsevier, Amsterdam–Oxford–New York–Tokyo (1986).
14. Z. Jia, A. O. Simm, X. Dai and R. G. Compton, *J. Electroanal. Chem.*, **587**, 247 (2006).
15. J. Newman, *J. Phys. Chem.*, **70**, 1327 (1966).
16. Y. H. Cheh and R. Sard, *J. Electrochem. Soc.*, **118**, 1737 (1971).
17. V. V. Losev, *Modern Aspects of Electrochemistry* (Eds. J. O'M. Bockris and B. E. Conway), Vol. 7, Chapt. 5, Butterworths, London (1972).
18. A. Alin, *Acta Chem. Scand.*, **11**, 1445 (1957).
19. B. Lovreček, I. Mekjavić and M. Metikoš-Huković, *Standard Potentials in Aqueous Solution* (Eds. A. J. Bard, R. Parsons and J. Jordan), Chapt. 5, Marcel Dekker Inc., New York–Basel (1985).
20. J. Emsley, *The Elements*, Clarendon Press, Oxford (1991).

**Ignas Valsiūnas, Laima Gudavičiūtė,
Vidmantas Kapočius, Antanas Steponavičius**

Bi ELEKTROLITINIS NUSODINIMAS ANT Pt RŪGŠČIOSE TERPĖSE 2. HIDRODINAMINĖ VOLTAMPEROMETRIJA

Santrauka

Pt sukamas disko elektrodas panaudotas gauti informaciją apie Bi elektrolitinio nusodinimo iš rūgštaus perchloratinio tirpalo 1 M HClO_4 + 0,05 M $\text{Bi}(\text{ClO}_4)_3$, kai temperatūra 20°C, procesą. Bi elektrolitinis nusodinimas iš šio tirpalo gali būti interpretuojamas taikant stadijinio Bi^{3+} jonų išsikrovimo modelio šitokius variantus: (i) išsikrovimų per tris vienelektronines stadijas su pirmojo elektrono pernešimu kaip reakcijos greitį limituojančia stadija, arba (ii) per dvi stadijas, kai pirmųjų dviejų elektronų pernešimas laikytinas reakcijos greitį limituojančia stadija. Remiantis gautais eksperimentiniais duomenimis, apskaičiuotas Bi^{3+} jonų difuzijos koeficientas D , kuris lygus $4.9 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.