

# Bi electrodeposition on Pt in acidic medium

## 1. A cyclic voltammetry study

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Electrodeposition of Bi onto Pt electrode was investigated in aqueous  $xM$   $Bi(ClO_4)_3 + 1M HClO_4$  solutions, where  $x = 0.001, 0.01, 0.05$  and  $0.1$ , using the cyclic voltammetry technique in a range of potential sweep rates from  $5$  to  $100\text{ mV s}^{-1}$ . The variations of the height and potential of cathodic current peak with changing the duration of cycling, sweep rate and concentration of  $Bi^{3+}$  ions were established. Analysis of experimental relationships among these quantities has indicated that they do not wholly satisfy the diagnostic criteria for simple reversible or totally irreversible reactions predicted by cyclic voltammetry theory. It was suggested that charge transfer in the system under question should be a more complex process involving a sequence of several separate steps, among which chemical or surface redox reactions are thought to occur. It was also established that, upon sweep reversal, the current trace crosses the forward (negative) sweep indicating the presence of nucleation overpotential.

**Key words:** bismuth, electrodeposition, perchlorate solutions, Pt electrode, cyclic voltammetry

### INTRODUCTION

Bismuth is a semimetal with unusual thermal, electrical and magnetic properties. Interest in bismuth is largely due to its small carrier effective mass and hence high mobility. Bi exhibits a very low carrier concentration and long carrier mean free paths leading to a very large magnetoresistance (MR) effect in bulk single crystals and in thin films grown by, in particular, electrodeposition. Therefore, Bi has attracted considerable attention for its actual and potential applications involving field and current sensing [1, 2].

By electrodeposition, it is convenient to control the properties of metal layer via changing electrolyte concentration, current density, potential and other experimental conditions. Electrodeposition is a simple, reproducible and effective route to deposit a metal layer with a desired microstructure and morphology.

However, comparatively little work has been published on fundamental and kinetic knowledge of bismuth electrochemical behaviour at various substrates. Electrical double layer (EDL) characteristics of Bi have been recently studied [3, 4], in particular, in terms of the Debye length-dependent roughness theory [3].

It has been found that bulk Bi and thin Bi films differ in some properties controlled by the carrier concentration and mobility. In bulk Bi, the carrier mobility dominates, whereas in Bi thin films the carrier mobility is suppressed by structural imperfections and probably finite-size effects, leading to a larger contribution of carrier concentration. Such a competition between these features has been suggested to cause different values of the temperature coefficient of resistance (TCR) for bulk Bi and Bi thin films [1].

Thin Bi films have been grown on mica, and the lattice parameters have been measured by XRD [5-7] and AFM [8]. The structural properties of Bi nanowires electrodeposited onto polycarbonate membranes have been characterised by the XRD and SEM techniques [1]. The size of particle and the morphology of Bi layer deposited onto Pt, Au, Al and indium-tin oxide (ITO) electrodes have been shown to be dependent on electrodeposition conditions using SEM and TEM imaging [2]. The Bi structural properties have been correlated with the magnetoresistance parameters [1, 2]. The similarity of the XRD patterns from polycrystalline thin Bi films deposited in acidic nitrate and alkaline trilonate solutions has been established [9]. It has recently been shown that significant bulk Bi deposition starts at a potential  $80\text{ mV}$  more negative than the Nernst reversible potential, and also that bulk Bi deposition is reversible

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[10]. *In situ* STM imaging has revealed a very interesting growth of Bi on Au substrate [10]. The presence of wide monoatomic-height areas during the early stages of electrodeposition of Bi onto Au and the absence of nucleated Bi islands on them suggest a slower nucleation rate on the Bi-covered parts of the substrate. A very different surface morphology was observed when the potential was slowly swept cathodically into the overpotential (OPD) region [10]. In this case, the growth was initially slow, followed by a faster 3D film growth that resulted in an amorphous film.

Comparatively little work has been published on the voltammetric characteristics of Bi electrodeposition onto various electrodes [11–14]. The current–potential relation of Ti electrode in nitrate Bi(III) solution has been shown to exhibit the limiting current which increased linearly with an increase in  $\text{Bi}(\text{NO}_3)_3$  concentration [11]. Thus, the observed limiting current is a diffusion current for a process limited by diffusion of  $\text{Bi}^{3+}$  ions. In contrast to the conclusion on the reversibility of the bulk Bi deposition [10], another author [12] has found that the reaction  $\text{Bi}^{3+} \rightarrow \text{Bi}^0$  is of poor reversibility. Because of this, after a few sweep cycles, the Bi film does not completely dissolve oxidatively, and a “ghost image” is left on the ITO electrode. The rest potential and the mass transport-limited region have been identified for Bi deposition in  $\text{Bi}(\text{NO}_3)_3$  solution onto a Bi electrode using voltammetry [13]. By stepping from the rest potential to a potential at which reduction of  $\text{Bi}^{3+}$  ions occurs, it has also been established that the Tafel region is narrow, and that the magnetic field increases the current in the long-time limit, *i.e.* in the Cottrell region [13]. One reduction wave and one oxidation wave have been observed for a Pt electrode in  $\text{Bi}(\text{NO}_3)_3$  solution [14]. After applying potentials more negative than a cathodic peak potential (*ca.*  $-0.080$  V *vs.* SSCE for  $0.0075$  M  $\text{Bi}(\text{NO}_3)_3$  solution), a dark deposit was formed. Since the identity of the deposit has been determined to be elemental Bi by XRD, the cathodic peak is assigned as the reduction of  $\text{Bi}^{3+}$  to Bi [14]. The anodic wave was assigned to the reverse of this reaction.

As one can readily see, these voltammetric experiments were confined, however, to a somewhat restricted range of conditions. As a consequence, the results obtained seem to be still far from systematic and sufficient for a deeper understanding of the voltammetric behaviour of the  $\text{Bi}^{3+}/\text{Bi}^0$  system. In this communication, the elucidation of the voltammetric features of this system will be made. We were primarily interested in such aspects of  $\text{Bi}^{3+}/\text{Bi}^0$  voltammetry as the reversibility of the redox reaction, the estimation of kinetic parameters and the determination of experimental conditions favouring the study of the early stages of Bi electrodeposition onto a foreign substrate.

## EXPERIMENTAL

Solutions were prepared using bismuth oxide  $\text{Bi}_2\text{O}_3$  (highest purity), perchloric acid  $\text{HClO}_4$  (chemically pure) and twice distilled water. All chemicals were used as received. The working solutions containing  $0.001$ ,  $0.01$ ,  $0.05$  or  $0.1$  M  $\text{Bi}^{3+}$  in  $1$  M  $\text{HClO}_4$  were applied for electrochemical measurements. Relating the nature of the Bi species present in acidic medium, it has been stated [15, 16] that for the concentration of  $\text{H}^+(\text{c}_H^+)$  more than  $0.4$  M, the aqua  $\text{Bi}^{3+}$  prevails ( $>97\%$ ) and that the hydrolysed forms such as a simple complex  $\text{Bi}(\text{OH})^{2+}$  and a polynuclear complex  $\text{Bi}_6(\text{OH})^{6+}_{12}$  are present in minor amounts. Prior to each experiment, the working solutions were deaerated with argon.

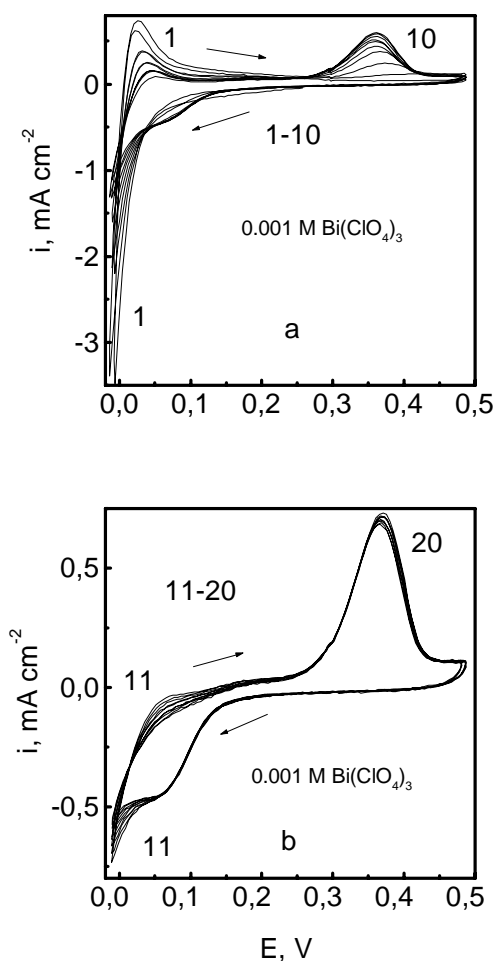
All experiments were carried out at a temperature of  $20 \pm 0.1$  °C in a conventional three-electrode cell. The working electrode was a vertical Pt disc of  $1$  cm<sup>2</sup> geometric area, made from a mat polycrystalline Pt foil (99.99% purity) and insulated with glass. The electrode was mechanically polished with diamond paste to  $0.5$  μm, further cleaned with octane and finally with magnesium oxide MgO powder. Prior to each experiment, the electrode was rinsed with  $\text{H}_2\text{SO}_4 + \text{HNO}_3$  (1:1) solution and then thoroughly with twice-distilled water. A Pt sheet  $6$  cm<sup>2</sup> in area was a counter-electrode. A saturated sodium silver–silver chloride electrode (SSCE) was used as a reference. In order to avoid the contamination of the working  $\text{Bi}^{3+}$  solution with  $\text{Cl}^-$  ions, the SSCE was connected to the electrochemical cell through a  $1$  M  $\text{HClO}_4$  bridge. The potentials reported in this paper are quoted *versus* the standard hydrogen electrode (SHE).

Electrochemical measurements were carried out using a PI 50-1 potentiostat (made in Belarus) interfaced through a home-made analogue to a digital converter with a PC (Siemens) and a PR-8 programmer (made in Belarus). The experimental data acquisition was in a numerical form with time resolution of  $4$  or  $50$  ms per point.

Bi was electrodeposited under potential control by a cyclic voltammetry (CV) technique. In these experiments, the working Pt electrode was first held at a rest potential ( $E_{\text{rest}}$ ) of *ca.*  $+0.240$  V for  $1$  min, and then a Pt electrode potential was scanned to a positive direction at a potential scan rate ( $\nu$ ) of  $50$  mV s<sup>-1</sup> to a switching anodic potential ( $E_{\text{sa}}$ ) of *ca.*  $+0.56 \pm 0.02$  V and back to  $+0.29$  V at which the subsequent cyclic voltammograms (CVs) started to be registered, *i.e.*  $E_{\text{start}} = +0.290$  V. Without any interruption, the Pt electrode potential was further cathodically scanned to the switching cathodic potential ( $E_{\text{sc}}$ ), but now at a designated value of  $\nu$ . The potential cycling programme applied here included variations in  $E_{\text{sc}}$  and in the number of cycles ( $n$ ).

## RESULTS AND DISCUSSION

Fig. 1 shows the effect of the Pt electrode consecutive cycling on the complete voltammetric profile ta-

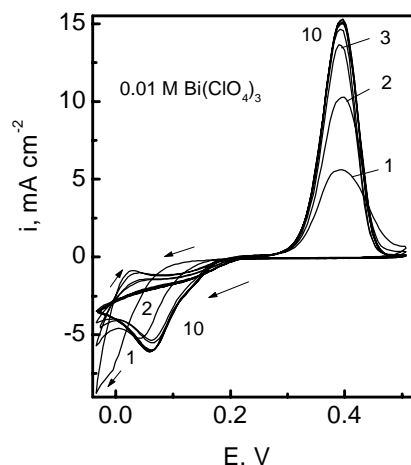


**Fig. 1.** Successive cyclic voltammograms (20 cycles) for a Pt electrode in acidic perchlorate 0.001 M  $\text{Bi}^{3+}$  solution at  $50 \text{ mV s}^{-1}$ . From the 1st to 10th cycle (a) and from 11th to 20th cycle (b)

ken over a potential region from *ca.* +0.48 V, as mentioned above, to *ca.* 0.00 V in 0.001 M  $\text{Bi}(\text{ClO}_4)_3$  solution. As can be seen, the form of the potential-dynamic profiles progressively changes for a succession of 20 cycles. During the cathodic scan, a shoulder-like portion of the voltammetric curve is rather easy to distinguish in an approximate potential region from +0.04 to 0.00 V, but at the same time it becomes narrower with increasing the number of cycles. Because of its rather indistinct shape it was impossible to measure accurately the peak potential ( $E_{pc}$ ). The anodic current peak appears clearly at +0.35 V during the continuous cycling. The height of this current peak attains an almost constant magnitude after 8–10 cycles. In contrast, the second anodic current peak at *ca.* +0.025 V reduces with increasing *n* and after 8–10 cycles disappears at all. Such a dependence of the height of the second ano-

dic current peak on the number of cycles appears to be caused by the changes in the kinetics and mechanism of Bi electrocrystallization and, consequently, in the structure of the very thin Bi(0) layer and in the following stripping process.

It can be noted that the shape of voltammetric curves recorded here (Fig. 1) somewhat differs from that presented recently by other authors [2]. In particular, in the cited reference, two reduction current peaks have been observed on a Pt electrode at about +0.25 and +0.05 V when a CV was recorded at  $50 \text{ mV s}^{-1}$  by a single scan in a potential region from +0.75 to -0.45 V in 0.001 M  $\text{Bi}(\text{NO}_3)_3$  solution. These cathodic current peaks have been suggested to correspond to the reduction reactions from  $\text{Bi}^{3+}$  to  $\text{Bi}^+$  and finally from  $\text{Bi}^+$  to Bi, respectively. The difference between the shapes of CVs recorded in our study (Fig. 1) and presented by other authors [2] seems to result from a different nature of the anionic composition of working solutions. Moreover, the mentioned dissimilarity can also be caused by different amplitudes of the potential cycling regions.

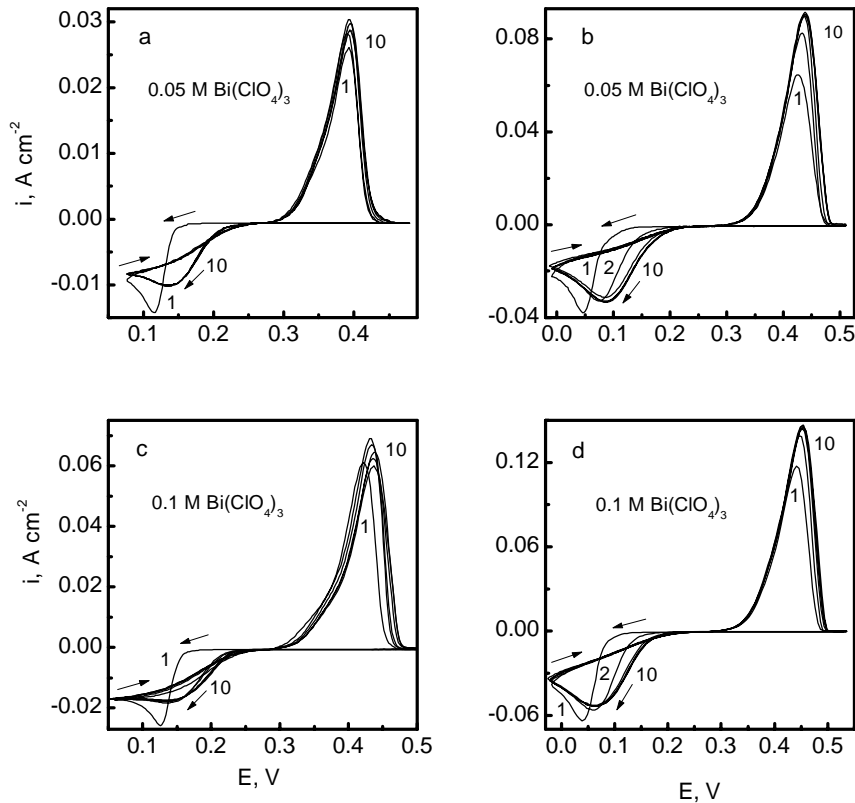


**Fig. 2.** The same as in Fig. 1, but in 0.01 M  $\text{Bi}^{3+}$  solution with 10 cycles

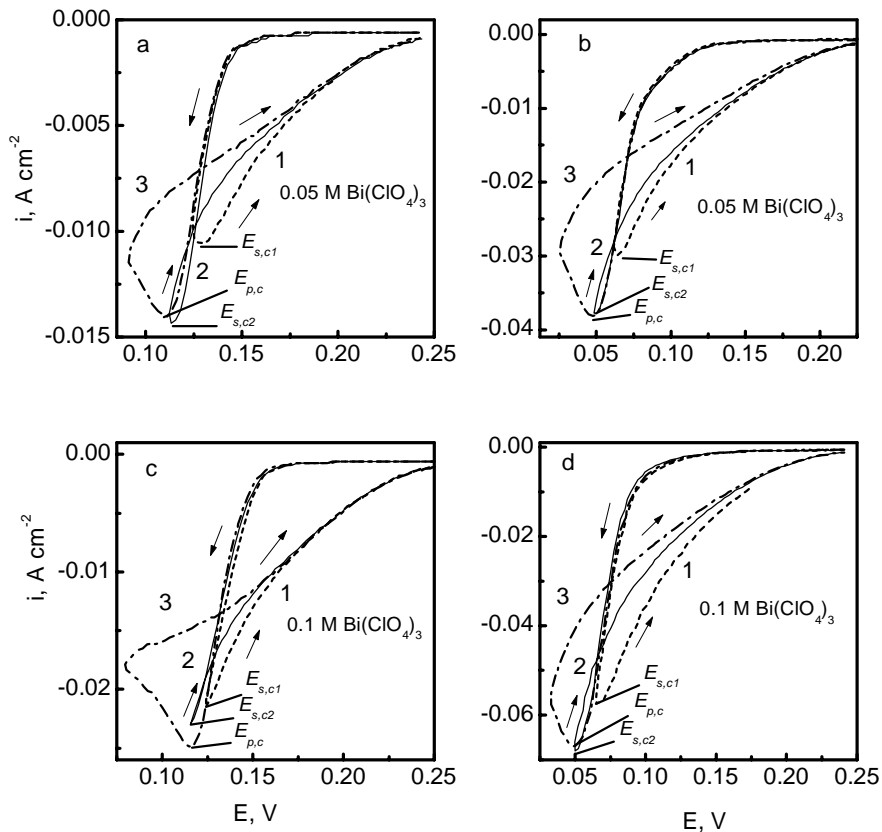
With increasing the bulk concentration of  $\text{Bi}^{3+}$ , the voltammetric curves recorded in our study (Figs. 2–4) acquire a form commonly expected for cyclic voltammetry [17]. One reduction wave and one oxidation wave, both having a distinct shape of current peaks, are observed for 0.01 (Fig. 2), 0.05 and 0.1 M  $\text{Bi}(\text{ClO}_4)_3$  (Figs. 3, 4) solutions. Bearing in mind the values of equilibrium potentials for a couple  $\text{Bi}^{3+}/\text{Bi}$  determined under similar or close experimental conditions [2, 18, 19] and also the values of potentials corresponding to the onset of bulk deposition of Bi [2, 10, 12], we tentatively assigned the reduction peaks to a reaction:



When an electrochemical reaction involves a transfer of more than one electron, it is usually conside-



**Fig. 3.** Successive cyclic voltammograms for a Pt electrode in 0.05 M  $\text{Bi}^{3+}$  (a, b) and in 0.1 M  $\text{Bi}^{3+}$  solutions (c, d) at  $5 \text{ mV s}^{-1}$  (a, c) or at  $50 \text{ mV s}^{-1}$  (b, d) with 10 cycles



**Fig. 4.** The same as in Fig. 3, but with reversal at more positive potential and with 3 cycles

red that several elementary stages are involved and that intermediates, which are generated as a result of charge transfer, may be adsorbed onto an electrode surface and, consequently, may give rise to an adsorption pseudo-capacitance. Then, one of the most important questions which must be addressed regarding the subject matter in our study is whether the overall reaction (1) proceeds through a single three-electron step, or multistep consecutive charge transfers should be taken into account. This point will be studied in our further work. At this stage, it is of main interest to investigate the voltammetric features of electrochemical deposition of Bi onto Pt from perchlorate  $\text{Bi}^{3+}$  solutions under potential-controlled conditions.

In our experiments, the value of the anodic and cathodic peak potential separation,  $\Delta E_p = E_{p,a} - E_{p,c}$ , for CVs after no less than 10 cycles at a given  $v$ , say, at  $50 \text{ mV s}^{-1}$ , equals 0.300, 0.332, 0.369 and 0.395 V for 0.001, 0.01, 0.05 and 0.1 M  $\text{Bi}(\text{ClO}_4)_3$  solutions, respectively, demonstrating that these values of  $\Delta E_p$  significantly exceed the quantity characteristic of a reversible process,  $\Delta E_p = 0.059/n$  at  $25^\circ\text{C}$  [17] and at  $n = 3$ . Then, tentatively assuming that a totally irreversible reaction may be the case, from the practically stabilized CV recorded, for example, in 0.05 M  $\text{Bi}(\text{ClO}_4)_3$  solution at  $v = 50 \text{ mV s}^{-1}$  (Fig. 3b), one can determine the magnitude of the product  $\alpha_c n_\alpha$ , where  $\alpha_c$  is the cathodic transfer coefficient and  $n_\alpha$  is the number of electrons transferred up to, and including, the rate determining step (rds). With this purpose, such a parameter of the selected CV as the shape factor  $|E_{p,c} - E_{p,c/2}|$  can be applied [17]:

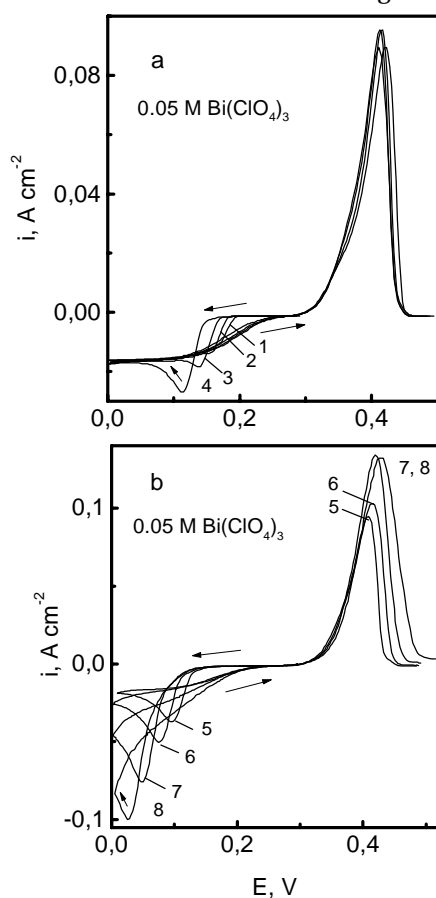
$$|E_{p,c} - E_{p,c/2}| = 0.048/\alpha_c n_\alpha \quad (2)$$

where  $E_{p,c/2}$  is the potential of a half-peak. It was found that  $\alpha_c n_\alpha = 0.94$ , if the reaction (1) is considered as totally irreversible.

It has also been known that on the basis of diffusion-controlled CVs a formal standard redox potential ( $E^0$ ) can be approximated by the mid-point potential of the anodic and cathodic peak potentials [17]. Regarding  $\text{Bi}^{3+}/\text{Bi}$  equilibrium, it should be noted that no reliable value of the standard potential ( $E^0$ ) for this couple is known. In particular, the values of  $E^0$  for the  $\text{Bi}^{3+}/\text{Bi}$  couple reported in the literature are in the range +0.20 to +0.32 V (SHE) [16, 19–21]. From the stabilised CV recorded here in 0.05 M  $\text{Bi}(\text{ClO}_4)_3$  solution at  $50 \text{ mV s}^{-1}$  ( $E_{p,c} = +0.069 \text{ V}$ ,  $E_{p,a} = +0.438 \text{ V}$ ), the formal standard potential  $E^0$  for the  $\text{Bi}^{3+}/\text{Bi}$  couple was found to be ca. +0.25 V.

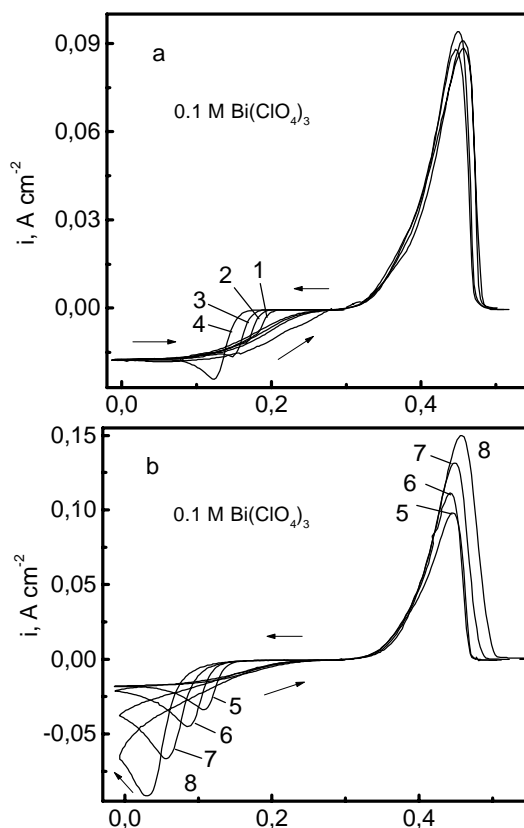
Also noteworthy is the occurrence of the hysteresis of CVs (the cathodic current is larger upon reversal of the potential scan), when an electrochemical window was narrowed by applying the value of  $E_{s,c}$  less negative than  $E_{p,c}$  (Fig. 4). Such a feature of CVs has been suggested to indicate a slow metal nucleation [22]. Preliminary experiments on this point for the system under discussion have already been performed recently [18].

Further investigations were made to establish the effect of the scan rate  $\nu$  on the height of cathodic

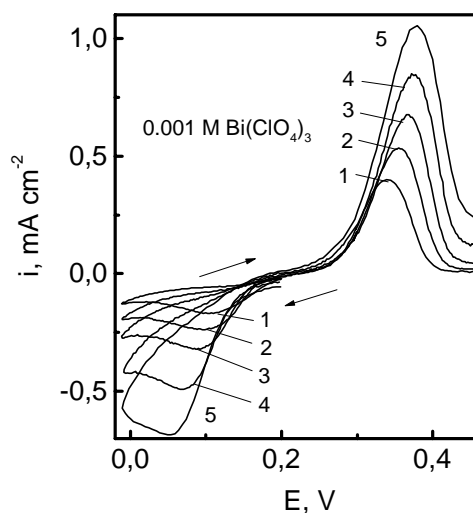


**Fig. 5.** Progressive change of profiles of cyclic voltammograms (the 1st scan) for Pt electrode in 0.05 M  $\text{Bi}^{3+}$  solution at a sweep rate in (a): 1 – 0.5, 2 – 1, 3 – 2 and 4 – 5  $\text{mV s}^{-1}$ ; in (b): 5 – 10, 6 – 20, 7 – 50 and 8 – 100  $\text{mV s}^{-1}$

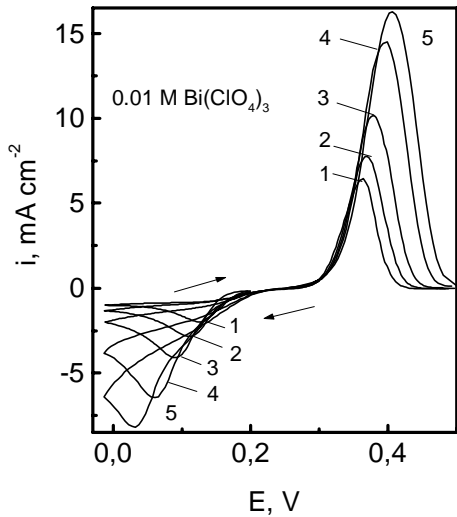
peak and the cathodic peak potential. The cathodic peak currents  $I_{p,c}$  were found to increase and the cathodic peak potentials  $E_{p,c}$  shifted negatively when  $\nu$  was increased during the first scan (Figs. 5, 6). The same picture is observed when the voltammetric responses are registered after  $n \geq 10$ , i.e. under the experimental conditions favouring the corresponding CVs to take a practically stabilised shape (Figs. 7–10). In either case, the peak currents were



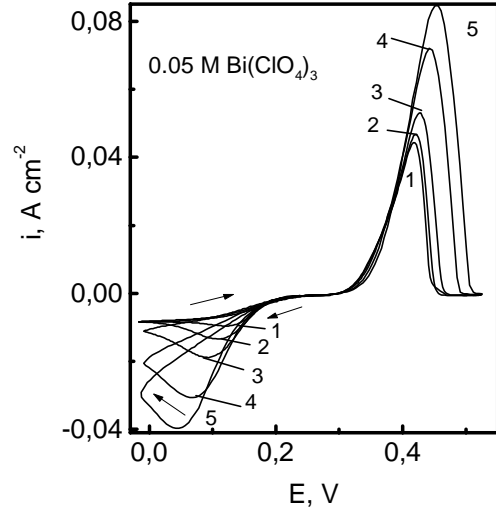
**Fig. 6.** The same as in Fig. 5, but in 0.1 M  $\text{Bi}^{3+}$  solution



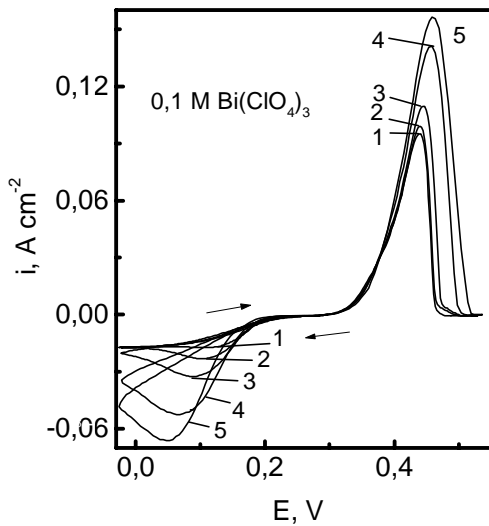
**Fig. 7.** Progressive change of profiles of cyclic voltammograms (after 20 cycles) for Pt electrode in 0.001 M  $\text{Bi}^{3+}$  solution at a sweep rate: 1 – 5, 2 – 10, 3 – 20, 4 – 50 and 5 – 100  $\text{mV s}^{-1}$



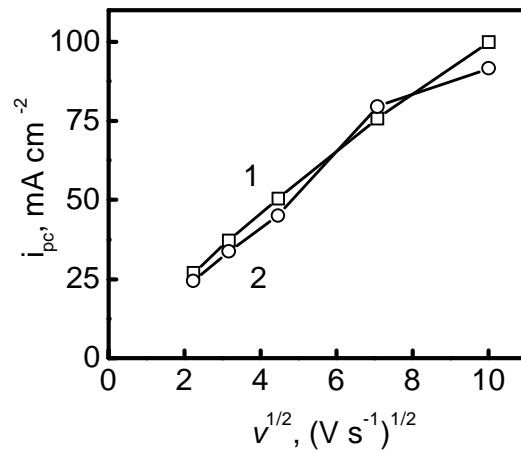
**Fig. 8.** The same as in Fig. 7, but after 10 cycles and in 0.01 M Bi<sup>3+</sup> solution



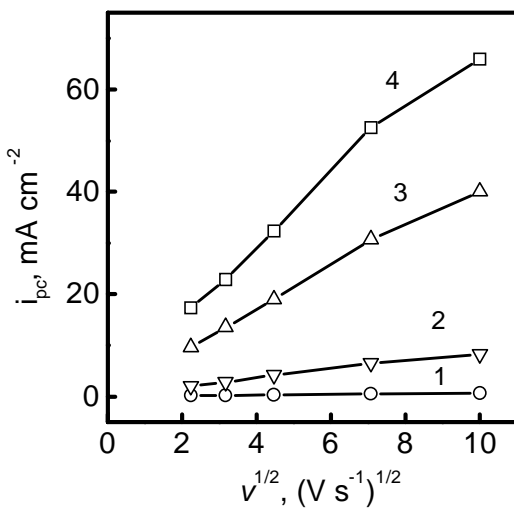
**Fig. 9.** The same as in Fig. 8, but in 0.05 M Bi<sup>3+</sup> solution



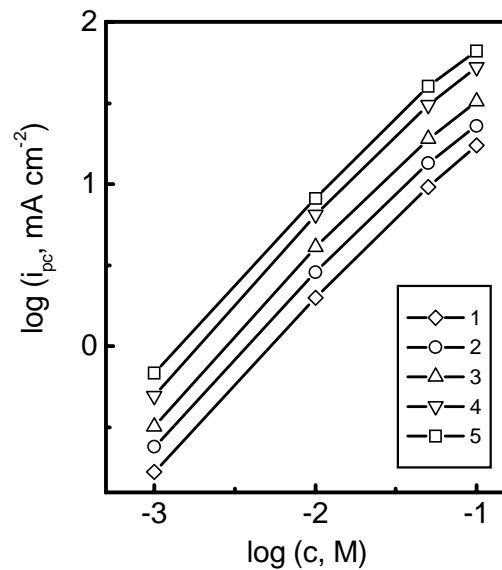
**Fig. 10.** The same as in Fig. 8, but in 0.1 M Bi<sup>3+</sup> solution



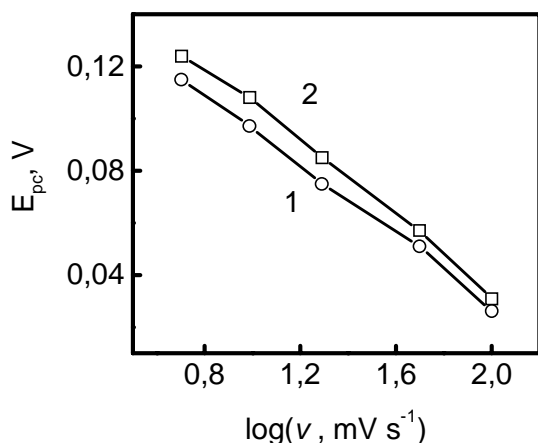
**Fig. 11.** Variation of the height of cathodic current peak with square root of potential sweep rate for the 1st scan in 0.05 (1) and 0.1 (2) M Bi<sup>3+</sup> solutions



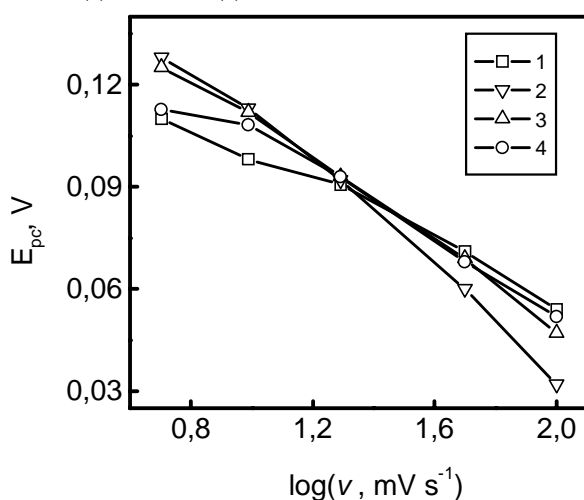
**Fig. 12.** Variation of the height of cathodic current peak with square root of potential sweep rate: 1 – after 20 cycles in 0.001 M Bi<sup>3+</sup> solution, 2 – 4 – after 10 cycles in 0.01 (2), 0.05 (3) and 0.1 (4) M Bi<sup>3+</sup> solutions



**Fig. 13.** Variation of the height of cathodic current peak with the bulk concentration of Bi<sup>3+</sup> (on a log-log scale) at the potential sweep rate: 1 – 5, 2 – 10, 3 – 20, 4 – 50 and 5 – 100 mV s<sup>-1</sup>. From the stabilized successive cyclic voltammograms



**Fig. 14.** Variation of the cathodic peak potential with the potential sweep rate (on a semi-log scale) for the 1st scan in 0.05 (1) and 0.1 (2) M  $\text{Bi}^{3+}$  solutions



**Fig. 15.** Variation of the cathodic peak potential with the potential sweep rate (on a semi-log scale) from the stabilized successive cyclic voltammograms in: 1 - 0.001, 2 - 0.01, 3 - 0.05 and 4 - 0.1 M  $\text{Bi}^{3+}$  solutions

found to be proportional to the square root of the sweep rate within the range of sweep rates applied (Figs. 11, 12) and to pass through the origin. One can see that the data obtained in the solutions with larger  $c$  of  $\text{Bi}^{3+}$  at  $100 \text{ mV s}^{-1}$ , *i.e.* at the largest value of  $v$  used in our experiments, begin to depart from linearity (Fig. 12, lines 3 and 4). Furthermore, within experimental error, the peak currents are also proportional to the bulk concentration of  $\text{Bi}^{3+}$  ions at a constant sweep rate (Fig. 13), where at a given value of  $v$ , say, at  $50 \text{ mV s}^{-1}$ ,  $(\partial \log I_{p,c} / \partial \log v) = 1.015$ ; in this case, a slight deviation from the linearity of these relationships, especially again at a larger bulk  $c$ , is not taken into account. The analogous  $I_{p,c}$  vs.  $c$  relationships for the 1st scan are not shown here.

The cathodic peak potentials  $E_{p,c}$  shift in the negative direction, as mentioned above, and are nearly linear with respect to the decimal logarithm of the sweep rate (Figs. 14, 15), suggesting that the reac-

tion (1) is not reversible and tentatively may be considered as irreversible. Then, from the variation of  $E_{p,c}$  with  $\log v$  given by the following equation [17, 23]:

$$E_{p,c} = K - (2.3RT/2\alpha_c n F) \log v, \quad (3)$$

where

$$K = E^0 - (RT/\alpha_c n F) [0.78 - (2.3/2) \log(\alpha_c n F D / k_s^2 RT)], \quad (4)$$

$k_s$  is the standard rate constant,  $D$  is the diffusion coefficient and the other terms have their usual significance, it should be expected that  $E_{p,c}$  shifts by  $30/\alpha_c n$  mV for each decade increase in  $v$ . However, as is evident from Fig. 15, the experimental shift of  $E_{p,c}$  for the 0.01, 0.05 and 0.1 M  $\text{Bi}^{3+}$  solutions with increasing  $v$  from 10 to  $100 \text{ mV s}^{-1}$  is equal to 81, 65 and 41 mV, respectively. Quite apparently, such values of the negative shift of  $E_{p,c}$  for each decade increase in  $v$  are in a considerable excess of that expected for the totally irreversible reaction [17, 23]. In addition, the observed concentration-dependence of the  $E_{p,c}$  shift is not predicted by theory of CV for irreversible systems [17, 23]. These features of CVs recorded in our work (see, *e.g.*, Fig. 15) and also the presence of the reverse peak (Figs. 1–10) clearly show that the diagnostic criteria for a totally irreversible system reported in the literature [17, 23] are not wholly satisfied. Consequently, the reaction (1) could not be considered as a simple irreversible reaction.

After reversal, during the anodic potential scan, the current crosses the zero-current axis at a potential ( $E_{\text{cross}}$ ) dependent on the scan rate and also on the bulk concentration of  $\text{Bi}^{3+}$  ions. For example, the crossing potential shifts to a positive direction by 55 or 46 mV with a tenfold increase in the bulk  $c$  of  $\text{Bi}^{3+}$ , from 0.001 to 0.01 M or from 0.01 to 0.1 M, respectively, at  $50 \text{ mV s}^{-1}$ . The same quantities obtained at a lower  $v$ , say, at  $5 \text{ mV s}^{-1}$ , are 47 and 26 mV, respectively. All these  $E_{\text{cross}}$  are larger than those expected for the equilibrium potential ( $E_{\text{eq}}$ ) for the reaction (1). It is still not clear why the effect of the  $v$  change on  $E_{\text{cross}}$  depends on the bulk concentration of  $\text{Bi}^{3+}$  ions. While this effect in more diluted solutions was found to be quite marked, in the case of 0.1 M  $\text{Bi}^{3+}$  solution  $E_{\text{cross}}$  was practically independent of  $v$  in the range 5 to  $100 \text{ mV s}^{-1}$ .

On the basis of our investigations made to date we may, therefore, hypothesize that Bi electrodeposition from acidic  $\text{Bi}^{3+}$  solutions refers to a more complex process which can include, in particular, chemical or coupled surface redox reactions. We are aware that this hypothesis is rather uncertain, but there are a number of points to be elucidated to define the type of complexity. To this it must be added that the blocking effect caused by a product or products of separate stages of the overall com-

plex cathodic process seems to be ruled out, because, as may be inferred from Figs. 1–10, no “ghost residual” is left on the surface of the working Pt electrode during anodic scan. Fuller examinations on this point are now in progress and will be reported in our next papers.

## CONCLUSIONS

Electrodeposition of bismuth onto a platinum electrode has been investigated in aqueous acidic perchlorate  $\text{Bi}^{3+}$  solutions using the cyclic voltammetry technique. The dependence of the peak current and peak potential on the number of successive cycles, sweep rate and on the bulk concentration of  $\text{Bi}^{3+}$  has been established. It follows from the results obtained that the conventional relationships between the parameters of cyclic voltammograms and the conditions of experiments differ strongly from the diagnostic criteria for simple reversible and totally irreversible systems. It has been supposed that charge transfer in the  $\text{Bi}^{3+}/\text{Bi}$  system is a more complex process coupled with separate steps of chemical or surface redox reactions. Upon sweep reverse at potentials positive of a deposition peak potential, the current trace has been found to cross the forward sweep indicating the presence of the slow nucleation stage.

Received 7 July 2005

Accepted 18 October 2005

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## Bi ELEKTROLITINIS NUSODINIMAS ANT Pt RŪGĐEIOSE TERPĖSE 1. VOLTAMPERINIS TYRIMAS

### S a n t r a u k a

Bi elektrolitinis nusodinimas ant Pt elektrodo 1 M  $\text{HClO}_4$  tirpale, kuriame buvo 0,001, 0,01, 0,05 ar 0,1 M  $\text{Bi}(\text{ClO}_4)_3$ , tirtas taikant ciklinės voltamperometrijos metodą esant potencialo skleidimo greičiams nuo 5 iki 100  $\text{mV s}^{-1}$ . Nustatytos katodinės srovės smailės aukėio ir tos smailės potencialo priklausomybės nuo chronoamperovoltmetrinio ciklo skaičiaus, potencialo skleidimo greičio bei  $\text{Bi}^{3+}$  jonų koncentracijos. Ėio priklausomybių analizė parodė, kad jos neatitinka tų diagnostinių kriterijų, kurie pagal ciklinės voltamperometrijos teoriją turi būti numatomi nekomplikuotam grątamajam arba negrątamajam procesams. Padaryta prielaida, kad krūvio pernešimas tiriamojame sistemoje yra komplikuotesnis procesas, jungiantis kelias atskiras stadijas seką, tarp kurių, kaip manoma, gali vykti cheminės arba paviršiaus redokso reakcijos. Taip pat nustatyta, kad pakeitus potencialo skleidimo kryptą srovės eiga kerta katodinio skleidimo kreivės dalį. Tai yra būdinga nukleacijos virėtamptui.