

# Bi electrodeposition on Pt in acidic medium

## 3. Voltammetric and gravimetric responses

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Electrodeposition of Bi from acidic perchlorate  $\text{Bi}^{3+}$  solutions onto Pt was studied by means of electrochemical quartz crystal microbalance (EQCM) combined with cyclic voltammetry (CV). The results of the calculations of the deposits' molar mass  $M$  performed on the basis of gravimetric data showed that depending on the conditions of electrolysis, the obtained deposits could be roughly partitioned into two groups: (i) almost pure Bi deposits with the value of  $M$  close to the expected value of  $M$  for pure bulk Bi; (ii) deposits with  $M$  significantly exceeding the expected value of these characteristics. The conditions favourable to the formation of almost pure Bi overlayers were revealed. Among these conditions, the increase in the thickness of the deposits with the increase in the concentration of  $\text{Bi}^{3+}$  ions and in the amount of the charge consumed during the overall electrochemical reaction should be mentioned first. It was also shown, that under specific conditions of electrolysis, in addition to the deposited  $\text{Bi}^0$ , some other species, most likely O-containing Bi compounds, were present on the Pt substrate. The higher calculated  $M$  values were supposed to be due to the incorporation of these additional species.

**Key words:** bismuth, electrodeposition, perchlorate solution, cyclic voltammetry, EQCM

### INTRODUCTION

Bismuth is an important metal due to its unusual thermal, electrical and magnetic properties [1–3]. Therefore, Bi has attracted considerable attention, in particular its deposits obtained by electrodeposition [2–18]. However, comparatively few works have been published on the electrochemical behaviour of Bi and the mechanism of its electrodeposition on various substrates [3, 11, 12, 16–18]. In particular, the current-potential relation of Ti electrode in nitrate Bi(III) solution has been shown to exhibit the limiting current,  $i_{\text{lim}}$ , which increased linearly with an increase in  $\text{Bi}(\text{NO}_3)_3$  concentration [12]. Then it has been concluded that  $i_{\text{lim}}$  is a diffusion-controlled current. In contrast to the conclusion on the reversibility of the bulk Bi deposition process [11], other authors have found that the reaction



is of poor reversibility [13] or is not a simple reversible or a totally irreversible reaction [16, 17]. The electrodeposition of Bi from acidic solutions has been suggested to be interpreted in terms of an irreversible step-

wise discharge of  $\text{Bi}^{3+}$  ions proceeding either through three successive one-electron steps with the transfer of the first electron as the rate-determining step (rds) or via two successive steps with the transfer of two electrons in the first step as the rds [17]. Noteworthy, the electrode reaction of  $\text{Bi}^{3+}$  reduction to  $\text{Bi}^+$  and finally from  $\text{Bi}^+$  to  $\text{Bi}^0$  has been considered when the electrodeposition of Bi from nitrate Bi(III) solution onto different substrates was studied using the cyclic voltammetry, XRD and SEM techniques [3].

Considering the mechanisms of the electrode reaction (1) sometimes showing the presence of some unpredictable species, in this paper we are presenting a study aimed at the usage of the electrochemical quartz crystal microbalance (EQCM) technique and simultaneously the cyclic voltammetry (CV) in order to compare the results obtained by CV and EQCM and to propose a reasonable mechanism for Bi electrodeposition.

### EXPERIMENTAL

The 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. Working solutions containing 0.01, 0.05 or 0.1 M  $\text{Bi}^{3+}$  in 1 M  $\text{HClO}_4$  were used for the experiments.

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Considering the nature of the Bi species present in an acidic medium, it has been stated [19] that for the concentration ( $c$ ) of  $H^+$  of more than 0.4 M, the aqua  $Bi^{3+}$  prevails (>97%) and that the hydrolysed forms such as a simple complex  $Bi(OH)^{2+}$  and a polynuclear complex  $Bi_6(OH)_{12}^{6+}$  are present in minor amounts. Prior to each experiment, the working solution had been deaerated with argon for 0.5 h.

All the experiments were carried out at a temperature of  $20 \pm 0.1$  °C in a three-electrode cell. The working electrode was a planar vertical 2.45 MHz (in solution) AT-cut quartz crystal coated by ca. 0.5  $\mu m$  Pt layer using the magnetronic sputtering technique. According to the Sauerbrey's equation [20], for rigid deposits, the change in the resonant frequency of the oscillating crystal ( $\Delta f$ ) is proportional to the change in the mass ( $\Delta m$ ) per unit area of the working electrode. The relationship is linear as long as  $\Delta f$  is less than a few percent of the resonant frequency of the crystal. The equivalence is expressed as in [20, 21]:

$$\Delta f = - 2\Delta m f_0^2 / A(\mu\rho)^{1/2} = - K\Delta m, \quad (2)$$

where  $f_0$  is the fundamental resonant frequency (in Hz), which as mentioned above, was equal to 2.45 MHz (in liquid),  $A$  is the piezoelectric active area (0.5  $cm^2$ ),  $\mu$  is the shear modulus of the quartz ( $2.947 \times 10^{11}$   $g\ cm^{-1}\ s^{-2}$ ),  $\rho$  is the density of quartz ( $2.648$   $g\ cm^{-3}$ ), and  $K$  is the experimental mass coefficient. The holder was made from polystyrene. The approximate sensitivity of the QCM was estimated by a galvanostatic deposition of Cu layer from 0.5 M  $H_2SO_4$  + 1 M  $CuSO_4$  solution at 1 A  $dm^{-2}$  and was found to be equal to 34.1  $ng\ Hz^{-1}$  for  $A = 0.5\ cm^2$ . The frequency was measured with an accuracy of 1 Hz in 1.3 s intervals when the potential sweep rate ( $v$ ) was 10 and 20  $mV\ s^{-1}$  or an accuracy of 10 Hz in 0.25 s intervals with  $v = 50\ mV\ s^{-1}$ . The counter electrode was a Pt plate and the reference electrode was a Ag/AgCl/NaCl(sat.) electrode (SSSE). The SSSE compartment was separated from the electrochemical cell by a 1 M  $HClO_4$  bridge. All potentials are reported in accordance with the standard hydrogen electrode (SHE). The home-built EQCM circuit was based on a PI 50-1 potentiostat (made in Belarus), a PR-8 programmer (made in Belarus) and a frequency counter Č3-34 (Russia).

The experimental data of the measurements of the applied voltage, current and frequency were recorded in a numerical form and stored on an IBM PC. The typical responses of  $\Delta m$  with a successive scan of the potential are shown in Fig. 1. The obtained results show that the characteristics of  $\Delta m$  responses exhibit a practically similar picture, i. e., the features of  $\Delta m - t$  relationships do not depend on the previous experiment or, in other words, on the prehistory of the sample. In general, the voltammetric scans were recorded after the electrodes had stood in the solution for 30 seconds in the potential region positive for bulk deposition and then extended to the region of bulk deposition. For the

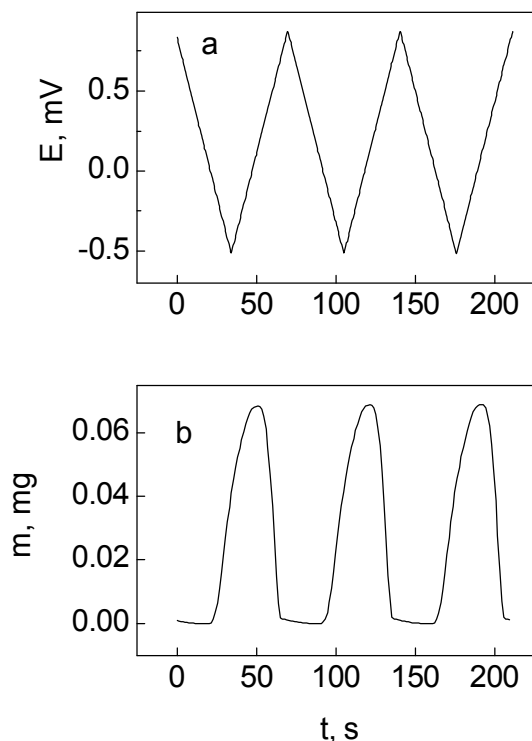


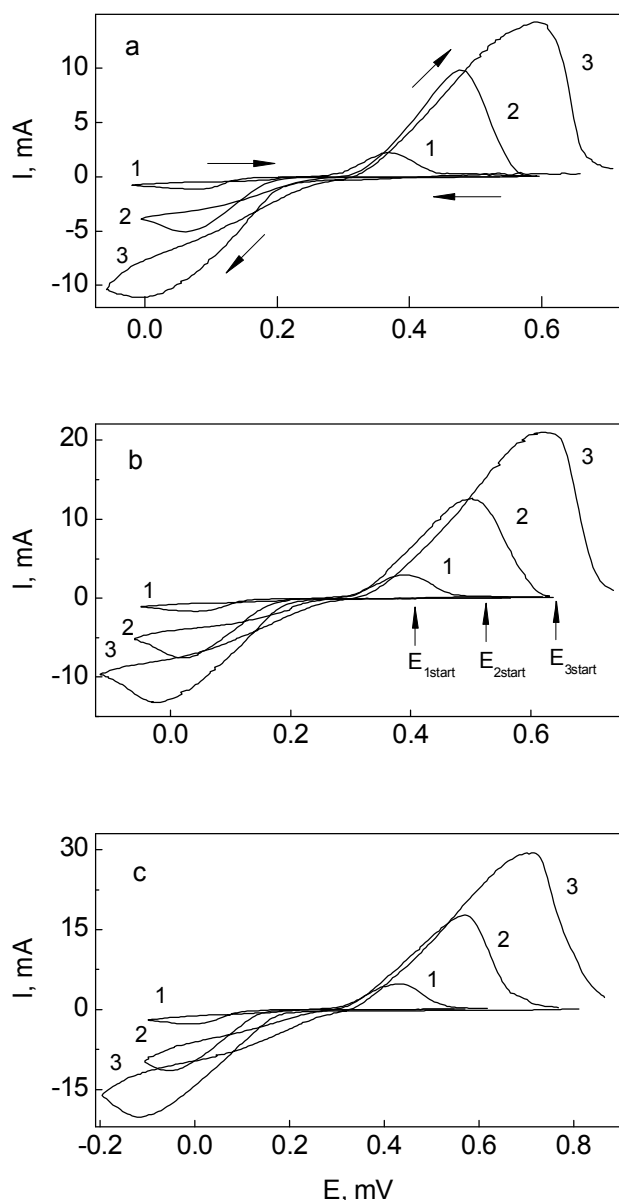
Fig. 1. Typical potential vs. time (a) and mass change vs. time (b) curves at potential scan rate of 20  $mV\ s^{-1}$  for Pt electrode in 1 M  $HClO_4$  + 0.05 M  $Bi^{3+}$  solution

systems considered here, the cathodic cycles proceeded after no less than 50 full cycles had been performed were used for the calculations.

## RESULTS AND DISCUSSION

Fig. 2 shows the stabilized cyclic voltammograms of the Pt electrode as a function of potential  $E$ , concentration of  $Bi^{3+}$  and also of potential scan rate  $v$ . It can be noted that the shape of the voltammetric curves recorded here are fairly similar to those presented in our earlier study [16]. Therefore, there is no need to discuss the features of these curves in detail.

Fig. 3 shows the comparison of the stabilized current vs. time curves, recorded voltammetrically (data from Fig. 2) and those calculated from the gravimetric measurements. It can be seen that in general, these  $i$  vs.  $t$  curves are relatively similar. A more significant difference between the corresponding pair of  $i$  vs.  $t$  curves occurs for the cathodic parts of the cycles with 0.1 M  $Bi^{3+}$  solution. In all the cases, the values of  $i$  measured gravimetrically are somewhat less than those obtained potentiodynamically. A more or less similar run of these two current traces seems to verify that the QCM responds as expected and, therefore, the oscillator frequency changes can be used for the preliminary assumptions on the mechanism of Bi electrodeposition. For a more convenient way of the following use of the gravimetric data, the  $i$  vs.  $t$  curves (dotted lines in Fig. 3) were replotted as  $m$  vs.  $t$  curves (Fig. 4).

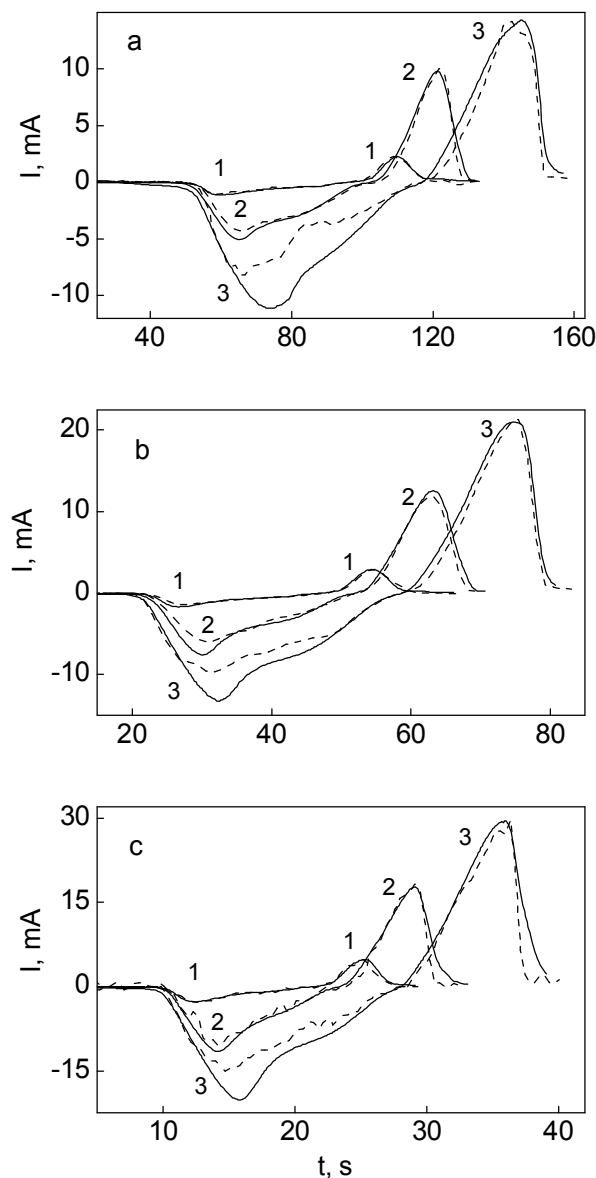


**Fig. 2.** Stabilized cyclic voltammograms (after no less than 50 cycles) for Pt electrode in 0.01 (1), 0.05 (2) and 0.1 (3) M Bi<sup>3+</sup> solutions at potential scan rate  $\nu$ : 10 (a), 20 (b) and 50 (c) mV s<sup>-1</sup>

The species involved in the electrochemical reaction on the substrate can be evaluated by combining the Sauerbrey equation (2) with the Faraday's law and plotting the quartz crystal frequency variation (i.e. the change in mass of the electrode) as a function of the charge  $q$  consumed during the reaction according to the equation:

$$\Delta f = - (KM / Fz)q, \quad (3)$$

where  $M$  is the molar mass of the deposit,  $F$  is the Faraday's constant and  $z$  is the number of electrons. The slope of the curve  $\Delta f$  vs.  $q$  is positive if a reductive current (negative  $q$ ) is accompanied by a frequency decrease, i.e. mass increase or deposition. An oxidative current (positive  $q$ ) is accompanied by a frequency in-



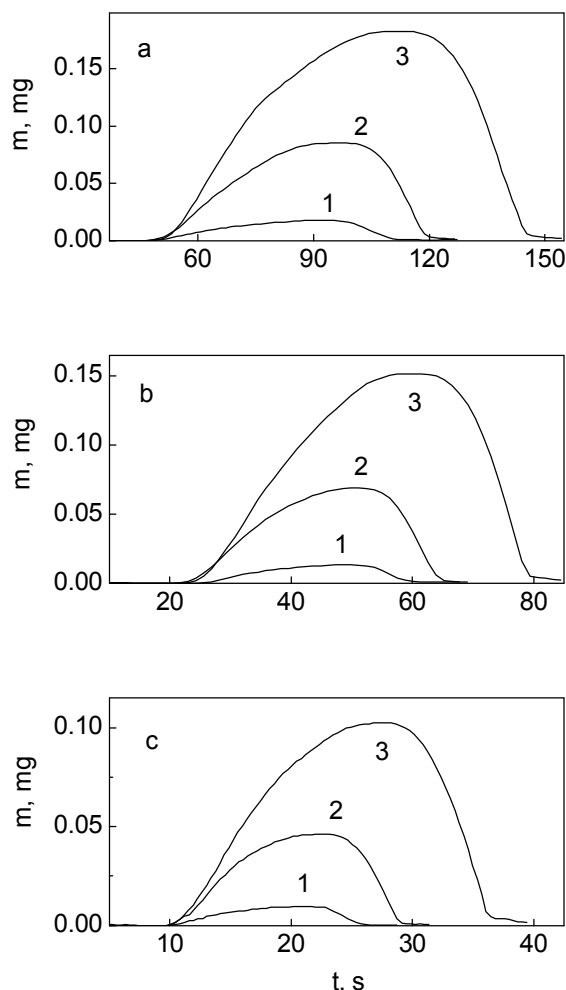
**Fig. 3.** Stabilized cyclic current vs. time curves for Pt electrode in 0.01 (1), 0.05 (2) and 0.1 (3) M Bi<sup>3+</sup> solutions at potential scan rate  $\nu$ : 10 (a), 20 (b) and 50 (c) mV s<sup>-1</sup>. Current values measured potentiodynamically (as in Fig. 2) (solid lines) and corresponding current values calculated from gravimetric measurements (dashed lines) and assuming that  $z = 3$

crease (mass decrease or dissolution). If no deposition or dissolution occurs in the electrochemical reaction ( $M = 0$ ), the slope is zero. For pure nonelectrochemical ( $q = z = 0$ ) deposition and dissolution reactions, including adsorption and desorption, the slope and the parameter  $M/z$  are infinite.

While assigning the slope of the  $\Delta m$  vs.  $\Delta q$  relationship to  $b$ , there is a possibility to highlight the changes that accompany the deposition process:

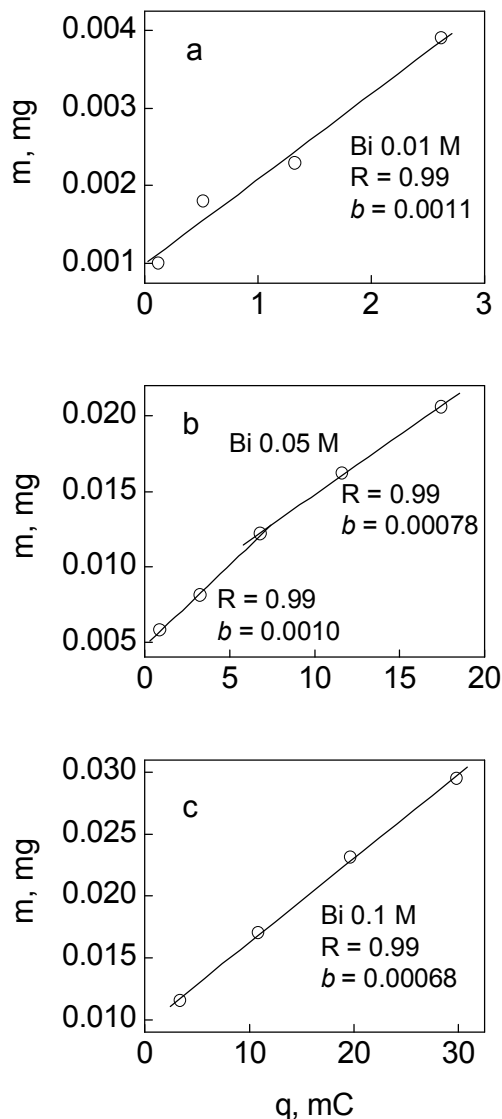
$$M = zF(\Delta m / \Delta q) = zFb \quad (4)$$

The experimental  $\Delta m$  vs.  $\Delta q$  relationship for the deposition of Bi onto Pt electrode calculated using the



**Fig. 4.** EQCM measurements on Pt showing the run of stabilized cycles with increasing and decreasing the added mass. Literal and numeral labelling as in Fig. 3

gravimetric data (the example presented in Fig. 4) are shown in Fig. 5. In accordance with Faraday's law, a linear relationship between the charge and the mass is rather well maintained, although the relationship for 0.05 M  $\text{Bi}^{3+}$  solution may be partitioned (Fig. 5b). From the analysis of the slope of each  $\Delta m$  vs.  $\Delta q$  relationship and considering that  $z = 3$ , it was found that in the case of 0.01 M  $\text{Bi}^{3+}$  solution at  $v = 10, 20$  and  $50 \text{ mV s}^{-1}$ , the apparent value of  $M$  is approximately 318. Such value significantly exceeds the molar mass of Bi ( $208 \text{ g mol}^{-1}$ ), but only formally is rather close to  $\text{Bi}(\text{OH})_3^{3-}$  ( $310 \text{ g mol}^{-1}$ ). While increasing the concentration of  $\text{Bi}^{3+}$  to 0.05 M or 0.1 M, the experimental  $b$  decreases (for 0.05 M  $\text{Bi}^{3+}$  solution at higher values of consumed  $q$ ) and, consequently, the quantity  $M$  becomes rather close to the expected value, in particular, ca. 200 to 225  $\text{g mol}^{-1}$ . The results indicate that: (i) there are some contributions from at least one of the other species on Pt in addition to  $\text{Bi}^0$ , (ii) the contribution of these species are more marked when the lesser amount of Bi is deposited onto Pt. Considering the  $M$  values determined here by the slope  $b$  of the fitting mass data as a function of the charge, it can be stressed that, to our know-



**Fig. 5.**  $\Delta m$  vs.  $\Delta q$  relationship for Bi deposition on Pt from 0.01 (a), 0.05 (b) and 0.1 (c) M  $\text{Bi}^{3+}$  solutions

ledge, there is no experimental evidence of the formation of a phase other than pure Bi. Nevertheless, our results indicate that at least one bismuth-rich phase in addition to pure Bi can be formed under the investigated conditions of the cathodic scan. Such additional phase seems to be due to the presence of oxygen.

Although mass changes are not sufficiently precise to enable the other contributions to be identified with certainty, some most obvious candidates can be identified. They include: (i) adsorbed hydroxide,  $\text{OH}_{\text{ads}}$  derived from  $\text{H}_2\text{O}$  in an acidic solution; (ii) solvent,  $\text{H}_2\text{O}$ . Thus, in order to explain the values of molar masses  $M$  calculated during the deposition of Bi in different regions of the consumed charge, i. e. in different regions of the thickness of the overlayer, we assume opposing transfers of  $\text{OH}_{\text{ads}}$  and/or  $\text{H}_2\text{O}$  in addition to  $\text{Bi}^{3+}$  ions. These transfers can play a more significant role in the cases of the very early stages of Bi deposition, including even Bi UPD process, 2D Bi crystallization and  $2\text{D} \rightarrow 3\text{D}$  transition onto Pt when the Bi overlayer is far from being compact.

Taking into account the whole results of EQCM and CV measurements presented here, a possible mechanism to interpret these results can be proposed considering that the mechanism of the electrodeposition of Bi onto Pt electrode from strongly acidic perchlorate solutions goes through at least two routes. The first route includes the participation of oxygenated Bi species and manifests itself during the very early stages of the deposition of Bi overlayer competing with the formation of almost pure bulk Bi layer from the diffusing  $\text{Bi}^{3+}$  species in  $\text{Bi}^{3+}$  solutions. The second route includes the formation of pure Bi deposits that are formed by the discharge of  $\text{Bi}^{3+}$  ions.

To gain some more insight into the mechanism of bismuth deposition from  $\text{Bi}^{3+}$  solutions onto Pt electrode, structural investigations are in progress.

## CONCLUSIONS

The reduction of bismuth ions onto Pt electrode in acidic perchlorate solutions appears to be characterized by two routes: (i) simultaneous competing reactions of the discharge of  $\text{Bi}^{3+}$  ions and O-containing Bi(III) species, most possibly adsorbed onto an electrode surface, taking place at the initial stages of the formation of the Bi overlayer; this route manifests itself in the  $M$  values significantly exceeding the values expected for the pure bulk Bi deposit; (ii) as the thickness of the Bi layer is increased with a particular increase in the concentration of  $\text{Bi}^{3+}$  and also due to the increase in the amount of the charge consumed during the electrochemical reactions, the  $M$  value decreases to the theoretical value predicted for direct Bi deposition from  $\text{Bi}^{3+}$  ions diffusing from the solution of bulk  $\text{Bi}^{3+}$ . These circumstances are suggested to be favourable for the formation of almost pure Bi layers.

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## Bi ELEKTROLITINIS NUSODINIMAS ANT Pt RŪGŠČIOSE TERPĖSE

### 3. VOLTAMPEROMETRINIAI IR GRAVIMETRINIAI ATSAKAI

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

Elektrocheminės kvarco kristalo mikrogravimetrijos ir ciklinės voltamperometrijos metodai pritaikyti tiriant Bi elektrolitinį nusodinimą ant Pt elektrodo iš rūgščių perchloratinių  $\text{Bi}^{3+}$  tirpalų. Dangų molekulinės masės  $M$  skaičiavimai pagal gautus mikrogravimetrinius duomenis parodė, kad priklausomai nuo elektrolizės sąlygų nusodintos dangos apytikriai yra dviejų grupių: (i) beveik grynos Bi dangos su  $M$  reikšme, artima gryno Bi  $M$  reikšmei; (ii) dangos, apibūdinamos  $M$ , kurios dydis gerokai didesnis už teorinę  $M$  gynam Bi. Nustatytos sąlygos, kurios yra palankios susidaryti beveik grynomis Bi dangoms. Tarp šių sąlygų visų pirma galima išskirti dangų storio didinimą dėl  $\text{Bi}^{3+}$  jonų koncentracijos didinimo ir dėl sunaudoto suminei elektrocheminei reakcijai elektros kiekio augimo. Taip pat parodyta, kad tam tikromis elektrolizės sąlygomis gautose dangose greta  $\text{Bi}^0$  ant Pt substrato yra kai kurios kitos dalelės, matyt, deguoniniai Bi junginiai. Padaryta prielaida, kad kur kas didesnės apskaičiuotosios  $M$  reikšmės gali būti susietos su šių papildomų dalelių įsiterpimu.