

Estimation of the composition of electrolytically prepared intermetallic bismuth–platinum deposits

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Abstract The method of partial anodic peak resolution is applied to complex voltammograms. The estimation of the composition of the intermetallic Bi–Pt compounds electrolytically deposited is carried out by a resolution of the components of the voltammograms. It is shown that non-equilibrium conditions take place in electrolytic Bi–Pt deposit when three intermetallic compounds such as: Pt₂Bi₃, PtBi₂, PtBi, and phase of pure Bi exist simultaneously on the electrode.

Keywords Bismuth · Platinum · Intermetallic compound · Binary alloy · Stripping voltammetry

Introduction

Stripping voltammetric determination of electrochemically inactive metal from its intermetallic compound is an important application of binary metal deposits. Estimation of the electrolytic coprecipitated sediments composition of two or more elements is a subject of special interest in stripping voltammetry, because coprecipitation and formation of

those intermetallics often changes the stripping signals of individual components.

Methods of phase analysis such as X-ray diffraction [1] are often not applicable for determination of electrolytic deposits composition because of limitations concerned with low quantity of electrodeposited phase (e.g., some electrolytic depositions may consist of 4...10 atomic layers only).

Even if determination of electro-inactive elements seems to be a difficult task, it becomes important nowadays, for instance, in case of platinum determination in ores. That is a particular task where stripping voltammetry can be applied because of its great accuracy and sensitivity. Sure it is not possible to obtain the anodic stripping peak of platinum electro-sediment [2]. Therefore, it is necessary to add another metal to obtain a coprecipitate with platinum on the electrode. It is known that Hg is utilized for this purpose [3]. However, it is a common tendency in electroanalysis to avoid use of toxic chemicals including Hg and its compounds. That is why non-toxic bismuth was chosen as a second metal for coprecipitation.

Coprecipitation of platinum and bismuth on the electrode surface results in formation of several intermetallic compounds. According to the bismuth–platinum phase diagram [4], bismuth and platinum can form three thermodynamically stable intermetallic compounds. Therefore, anodic stripping of the coprecipitate gives four significantly overlapped peaks. Apparently, further measurement of phase composition requires resolution of those peaks. That is where various methods of mathematical peak resolution can be applied.

Mathematical resolution of overlapped phase peaks allowed us to study the phase composition of binary electrolytic Bi–Pt deposits and gave us possibility to investigate Pt–Bi deposits formation at the electrode surface. There is a series of methods of a mathematical resolution of the complex signals. One of the most spread methods of a mathematical

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solution of overlapped peaks is curve fitting [5, 6]. The primal constraint of curve fitting method is that at increasing of number of single peak in complex signal change of computing scheme and increasing of number of optimized parameter are necessary. This brings to significant complicating of optimization problem.

The step-by-step mathematical resolution method (SMRM) of the complex signals was described [7]. This method has a few advantages, in particular: algorithmic simplicity of realization, universality, and possibility of resolution of multicomponent mixture signals in cases when shape of individual signals is unknown a priori. Thus, SMRM was used here.

Experimental part

Reagents and chemicals

All chemicals used were of analytical or pharmaceutical grade and solutions were prepared in deionizer water. Platinum, bismuth, and hydrochloric acid were supplied by Merck.

Electrochemical measurements

Voltammetric measurements were carried out with an analyzer TA-4 (“Tom’analit”, Tomsk) and a conventional two-electrode system was adopted and quartz glasses of $V=20$ ml as electrochemical cells. A polyethylene-impregnated graphite electrode served as working electrode. It was produced according to the method described in [8]. A saturated silver/silver chloride electrode served as reference; 0.05 HCl solution was used as a background electrolyte. Electrochemical deposition of binary deposits was carried out at -1.0 for 60 s from a solution containing PtCl_6^{2-} ions and bismuth (III). Electrochemical oxidation of deposits was recorded with linear-sweep voltammetry ($v=80$ mV s^{-1}) in the range from -0.2 V to 0.8 V.

Results and discussion

Figure 1 shows voltammograms of the electrochemical oxidation of a Bi–Pt deposit on graphite exhibiting four overlapping peaks. The peak potential of electrochemical oxidation of pure Bi occurs at $E_1=-0.05$ V. Three additional peaks following the addition of platinum (IV) ions to the solution. The peak of pure Bi decreases but the total area of all peaks is constant.

The processes of electrochemical oxidation of Bi–Pt deposits from the surface of indifferent graphite electrodes have not yet been described in literature. Therefore, we

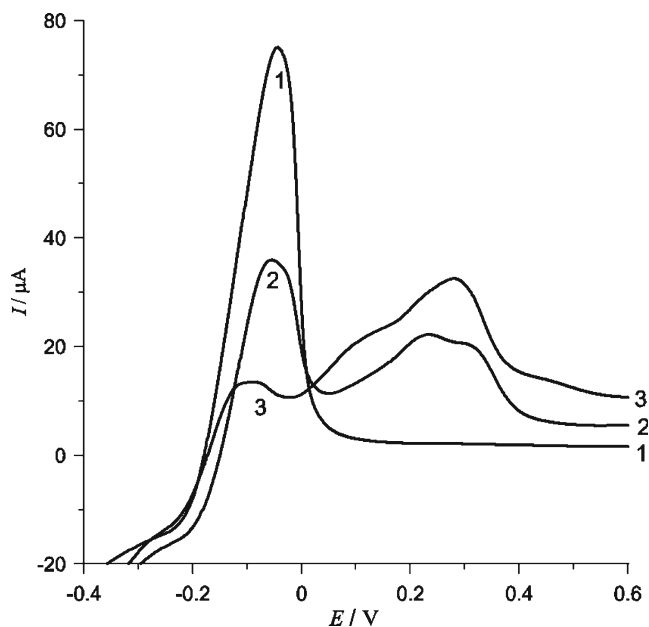


Fig. 1 Voltammetric curves of the electrochemical oxidation of a Bi–Pt deposit from the surface of graphite electrode. Experimental conditions, 0.05 M HCl solution; $\tau_e=60$ s, $v=80$ mV s^{-1} : 1 is the curve recorded in a pure bismuth ($1,000$ mg l^{-1}) solution, 2 is the curve recorded after the third addition of platinum (i.e., with a total concentration of 3 mg l^{-1} Pt(IV)), 3 is the curve recorded after the fifth addition of platinum (i.e., with a total concentration of 5 mg l^{-1} Pt(IV))

cannot give the exact interpretation of the additional peaks in the presence of Pt; however, it is known [3] that only those elements, e.g., Hg, can be oxidized from Pt co-deposits which are less noble than Pt. Therefore, we suppose that at the additional peaks there occurs the oxidation of Bi from different Bi–Pt phases. This assumption is supported by the experimental finding that the sum of areas under all peaks remains constant and equals the area under the peak of dissolution of pure Bi. The platinum is not oxidized; a fact that could be established from additional inspections of the electrode surface after oxidation of Pt: after dissolution of Bi the electrode was used to deposit mercury, and the following anodic dissolution voltammograms proved the presence of the well-known Hg–Pt dissolution voltammograms. In case of oxidation of Bi from Bi–Pt deposits, the only possibilities to get rid of the Pt are either a mechanical polishing or an electrochemical polarization at potential $+1.2$ V.

It was not possible to determine composition of the Bi–Pt phases by X-ray diffraction because of the very small amounts of substance deposited on the graphite electrodes. However, it is known from the literature [4] that the composition of electrochemical deposits often corresponds to phases described in known phase diagrams. According to the known Bi–Pt phase diagrams the following compounds can be formed: PtBi_2 , Pt_2Bi_3 , and PtBi [9]. The molar fractions of Bi in these intermetallic compounds are 0.66, 0.6, and 0.5, respectively.

According to the literature data the selective electrochemical oxidation of a less noble component from the alloy with a more noble metal takes place at a more positive potential compared to the oxidation potential of the pure metal. The difference may be rather significant and it is at maximum when diluted solutions are used for deposition, and also for ordered compounds (intermetallic compounds). The peak potential depends on the composition of the intermetallic compound.

In case of overlapping peaks it is difficult to determine the peak parameters of the individual peaks. Therefore, a mathematical resolution of peaks has to be performed.

The step-by-step mathematical resolution method was used here [7]. The main idea of this method consists in step-by-step mathematical removal of a signal of one substance from a complex signal. Thus signals of other components are available for the measurement.

The expression being a base of this method is as follow:

$$A_i = C_i - B_i, \tag{1}$$

where A_i — i th signal point on the voltammogram, C_i — i th signal point on the voltammogram, and B_i — i th signal point on the voltammogram (Fig. 2).

Before resolution illustration all curves were smoothed out. The calculation of residual current was carried out by means of splines to the extent 2.5 according to the methods described in the article [2].

Figure 3 shows original voltammetric curves and mathematically resolved partial peaks.

It is defined that potentials of additional peaks do not vary when the content of one of the alloy components varies. The area under all anodic peaks does not depend on the correlation of Pt and Bi in deposit.

It has been shown earlier [3, 10] that the peak potential shift for the electrochemical oxidation of the less noble component of intermetallic phases can be described by a

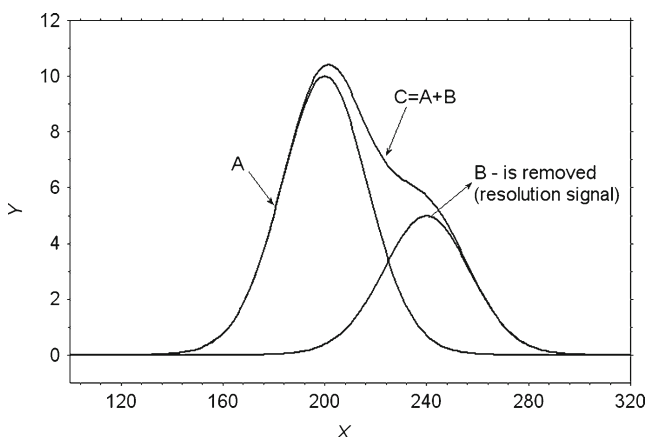


Fig. 2 Graphic illustration of step-by-step mathematical resolution method

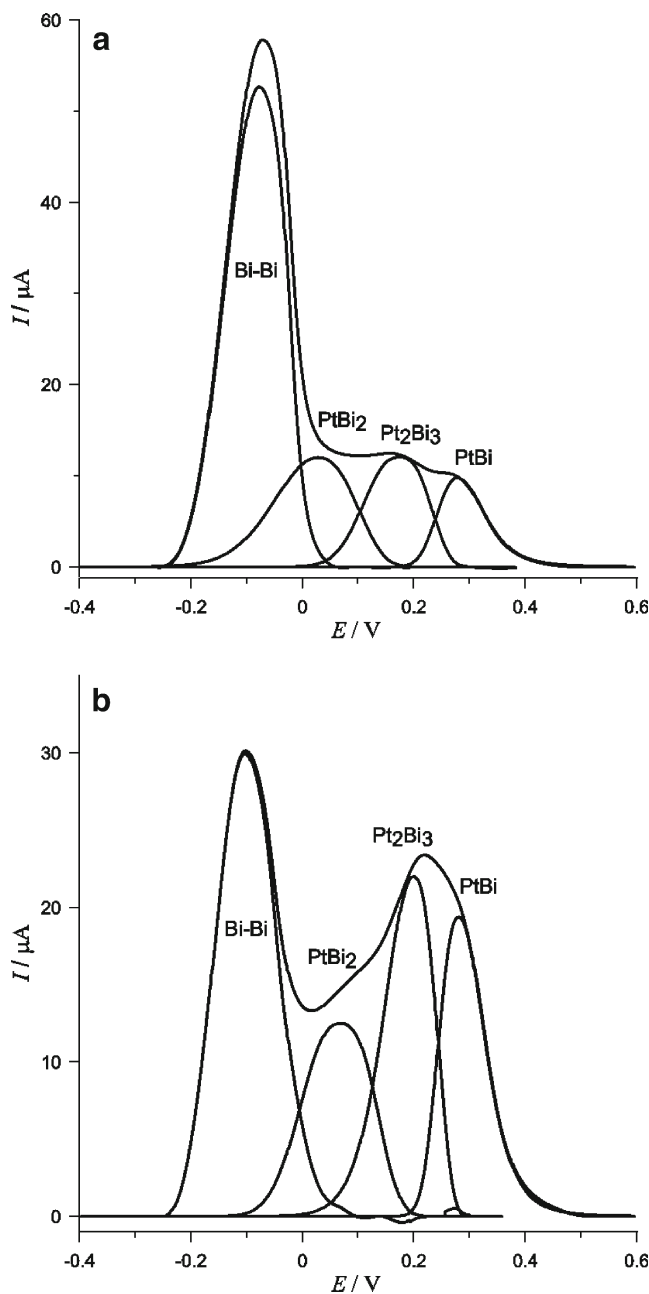


Fig. 3 Voltammetric curves of electrochemical oxidation of the bismuth-platinum deposit before and after resolution of partial peaks, **a** Bi-Pt=1,000: 1 mg l⁻¹; **b** Bi-Pt=1,000: 3 mg l⁻¹

general equation, which can be written in the special case of Bi-Pt as follows:

$$\Delta E_{paBi} = E_{paBi} - E_{paBi}^m = \frac{RT}{zF} \ln X_{Bi} - \frac{(1 - X_{Bi})}{zF} \epsilon_m, \tag{2}$$

where E_{paBi} is the anodic peak potential of pure bismuth (-0.05 V);

E_{paBi}^m is the anodic peak potential of oxidation of bismuth from the Bi-Pt alloys

ε_m is the integral mixing heat of the compounds forming the intermetallic phases
 X_{Bi} is a mole fraction of Bi.

The mixing heats of alloy formation can be approximately calculated from the energies of formation of covalent bonds between the metals using Pauling's correlation equation [11]:

$$\varepsilon_m = \frac{1}{2}(\varepsilon_{A-A} + \varepsilon_{B-B}) + 100(\chi_A - \chi_B)^2 - 6,5(\chi_A - \chi_B)^4, \quad (3)$$

where ε_{A-A} , ε_{B-B} are the energies of formation of the metallic bonds between A and B atoms, respectively; χ_A , χ_B are the electronegativities of the alloy components. The energy of the metallic bonds formation and the electronegativity values of elements are taken from the published data [12, 13]. The mixing heat of bismuth and platinum components calculated according to published data is equal to $386.5 \text{ kJ mol}^{-1}$.

With the help of Eqs. 2 and 3, one can calculate the peak potentials of bismuth oxidation from the different intermetallic phases and one can compare these data with the experimentally obtained data. Table 1 shows the comparison for five experiments in the range of platinum (IV) ions concentration from 1 to 5 mg l^{-1} .

As shown from the table there is a good correlation between calculated and experimentally defined values of peak potentials.

According to calculated potentials, one can make the following conclusion: at what potential bismuth selective oxidizes with platinum from every IMC: peak 2 ($E=0.08 \pm 0.03$) corresponds to the process of selective electrochemical oxidation of bismuth from IMC PtBi_2 ; peak 3 ($E=0.18 \pm 0.03$) is from IMC Pt_2Bi_3 ; and peak 4 ($E=0.28 \pm 0.02$) is from IMC PtBi .

Thus, the electrolytic bismuth–platinum deposit is a mixture of pure bismuth and IMC compounds of different composition.

The compounds are capable to selective electrochemical oxidation of IMC on the base of bismuth PtBi_2 , Pt_2Bi_3 , and PtBi .

Table 1 Comparison of the calculated and experimentally determined values of the potentials of the peaks of selective bismuth electro-oxidation from IMC containing platinum

Potential of an anodic peak of bismuth	Composition of IMC PtBi_2 $X_i=0.66$	Composition of IMC Pt_2Bi_3 $X_i=0.6$	Composition of IMC PtBi $X_i=0.5$
E_{calc} , V	0.1	0.17	0.29
E_{exp} , V ($P=0.95$; $n=5$)	0.08 ± 0.03	0.18 ± 0.02	0.28 ± 0.02

Two phases only should be in an electrolytic deposit under the conditions of equilibrium between phases (in case of bismuth excess, these phases should be Bi and PtBi_2). The voltammetric curves of electrochemical oxidation of bismuth should be observed as a subsequent transition from more enriched IMC with bismuth to less enriched. It is necessary to take into account that platinum from an electrode is not oxidized. Thus ratio of areas of partial peaks, corresponding to following transitions: $\text{PtBi}_2 \rightarrow \text{Pt}_2\text{Bi}_3$, $\text{Pt}_2\text{Bi}_3 \rightarrow \text{PtBi}$, $\text{PtBi} \rightarrow \text{Pt}$ should be 1:1:2. The total area under all peaks corresponds to quantity of bismuth in initial IMC (PtBi_2). Then the sum of partial peaks areas corresponding to electro-oxidation of bismuth from IMC should be a linear function from Pt (IV) concentration in solution (first hypothesis).

Some phases can be formed on the electrode under the conditions far from equilibrium. These phases will be present simultaneously in a fresh deposited electrolytic deposit. At the selective oxidation of these phases the quantity of the platinum connected with bismuth in various IMC will corresponds to quantity of oxidized bismuth in different ways. One should note the ratio between quantities of elements in IMC. Then the total quantity of platinum connected with bismuth is equal to sum of quantity of electricity corresponding to bismuth oxidation from first IMC multiplied by 1/2, from second IMC multiplied by 3/2, from third IMC multiplied by 1. The sum of partial peaks areas with taking into account the above mentioned coefficients should be a linear function of Pt (IV) concentrations in solution. The investigations carried out showed that equilibrium conditions practically are not observed in fresh deposited electrolytic deposit (second hypothesis).

For investigated Pt (IV) concentration range (from 1 to 5 mg l^{-1}) dependence of sum of partial peaks areas (with taking into account ratio of elements in IMC) has liner character (correlation coefficient $R=0.99$). The dependence of sum of partial peaks areas (without taking into account ratio of elements in IMC) has correlation coefficient $R=0.93$.

Non-observance of ratios between areas of partial peaks corresponding to electro-oxidation of bismuth from IMC indicates in favor of nonequilibrium condition (second hypothesis). Different range of ratios between areas of partial peaks is observed (from 2:1.5:1 to 1.5:1:3) in different experiments. These differences can be explained by different conditions of simultaneous formation of IMC phases thus confirming the hypotheses about the simultaneous availability of all three phases on electrode.

Conclusion

The method of resolution of partial anodic peaks from a complex voltammograms was applied. It is necessary take into account compositions of intermetallic compounds in

electrolytic bismuth–platinum deposits for correct electrochemical determination of platinum. It is shown then that intermetallic compounds such as PtBi₂, Pt₂Bi₃, PtBi, and phase of pure Bi exist simultaneously on the electrode.

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