

XV International Scientific Conference “Chemistry and Chemical Engineering in XXI century”
dedicated to Professor L.P. Kulyov

Anodic stripping determination of Pt (IV) based on the anodic oxidation of Cu from the intermetallic phase of Cu₃Pt

E.M. Ustinova^a*, N.A. Kolpakova^a

^a*Tomsk Polytechnic University, Lenin Avenue, 30, 634050, Tomsk, Russia*

Abstract

It is shown that platinum can be determined by anodic stripping voltammetry at the peak of selective electrooxidation of copper from intermetallic phase with platinum of Cu₃Pt composition. The composition of intermetallic copper-platinum phase formed on the electrode during pre-electrolysis was calculated on the amount of potential displacement (ΔE) of copper electrooxidation.

© 2014 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/3.0/>).

Peer-review under responsibility of Tomsk Polytechnic University

Keywords: copper, indium, platinum, intermetallic phase, binary alloy, stripping voltammetry, graphite electrode.

1. Introduction

It is known that deposits of platinum do not oxidize from the surface of a graphite electrode. When platinum is determined by stripping voltammetric methods^{1,2}, normally co-precipitations of other metals such as lead, mercury, etc. are used. It is expected that the presence of other metals on the electrode surface forms one or more intermetallic compounds with these metals. Previously we have shown that the determination of platinum, if precipitating it together with indium, is possible^{3,4}. In this paper we show the possibility to use copper as a metal activator. Copper with platinum in a solid phase forms a series of intermetallic compounds⁵.

The goal of this paper is to study the process of electrooxidation of Cu-Pt electrolytic deposit and calculate the composition of the Cu-Pt binary alloy.

* Corresponding author, tel.: +7-3822-606-210
E-mail address: Ustinova@tpu.ru

2. Experimental part

Voltammetric measurements were carried out with the analyzer TA-4 ("Tom'analit", Tomsk). A conventional three-electrode system with special quartz beakers of $V=20$ ml as voltammetric vessels was used. A polyethylene-impregnated graphite electrode produced according to⁶ was used as a process electrode. Saturated silver/silver chloride electrodes were used as reference and supporting electrodes. Platinum (IV) and copper (II) were precipitated from the solutions containing chlorides of these metals at the potential of -0.8 V. The graphite electrode was electrochemically cleaned by keeping it at 1.05 V for 60 s.

3. Results and discussion

Copper (II) was precipitated on the graphite electrode surface from the solution containing 1 mol L^{-1} of hydrochloric acid at the potential of -0.8 V. The anodic peak of copper was observed at -0.27 V. When platinum and copper are electrochemically precipitated together, only one peak is observed. Its potentials and currents depend on the concentrations of both platinum (IV) and copper (II) in the solution. Figure 1 shows the voltammograms of copper oxidation from copper-platinum alloys.

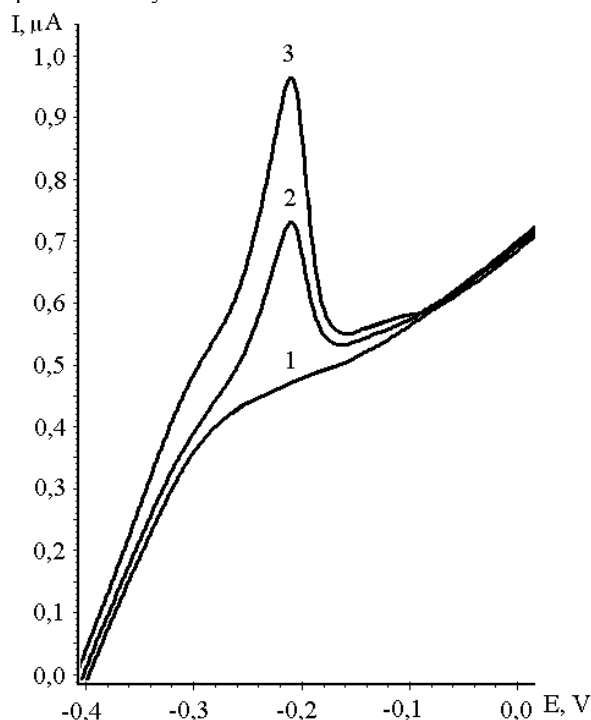


Fig.1. Voltammograms of electrochemical oxidation of copper-platinum alloys.

Experiment conditions: 1 mol L^{-1} of hydrochloric solution, deposition time $t_d = 100$ s, scan rate $v = 80 \text{ mVs}^{-1}$:

- (1) anodic stripping voltammogram of a pure hydrochloric solution (1 mol L^{-1}),
- (2) anodic stripping voltammogram after first addition of platinum (i.e. 1 mgL^{-1} Cu(II), 0.02 mgL^{-1} Pt(IV)),
- (3) after second addition of platinum (0.04 mgL^{-1}).

Figure 2 shows the dependence of the voltage of electrochemical oxidation of copper-platinum alloy on the concentrations of platinum (IV) in the solution.

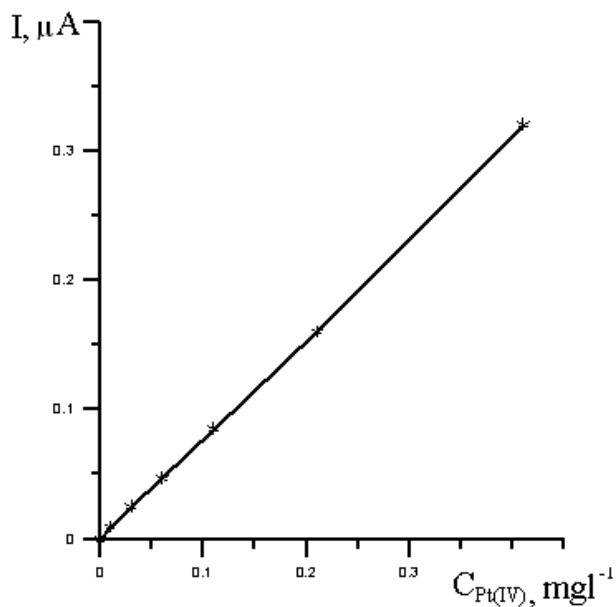


Fig.2. Dependence of the anodic peak current of copper on the concentration of platinum (IV) in the solution.
Experiment conditions: background – 1M HCl, $\tau_e = 80$ s, $C_{Cu(II)} = 1 \text{ mg l}^{-1}$

The resulting linear concentration range is used for determination of platinum ions in the solutions by stripping voltammetry.

When the Cu (II) and Pt (IV) contents of the solution vary, the individual peak currents of individual intermetallic compounds vary as well, but the peak potential remains constant. This is a strong indication of the invariant composition of these intermetallic compounds (constancy of composition).

It can be expected that the electrochemical oxidation of copper from different Pt-Cu phases (intermetallic compounds) will occur at anodic peaks at different potentials. According to literature data⁵, copper and platinum form the following intermetallic phases: Cu_3Pt , CuPt_7 , CuPt_3 , CuPt .

It has been shown earlier³ that the peak potential shift for electrochemical oxidation of less noble components of intermetallic phases can be described by a general equation, which can be written in special case of Cu-Pt as follows:

$$\Delta E_{\text{Cu}} = E_{\text{Cu}^{2+}/\text{Cu}}^0 - E_{\text{Cu}^{2+}/\text{Cu(Pt)}}^{\text{cm}} = \frac{RT}{z_{\text{Cu}}F} \ln X_{\text{Cu}} - \frac{(1 - X_{\text{Cu}})^2}{z_{\text{Cu}}F} \mathcal{E}_{\text{mix}}, \quad (1)$$

where $E_{\text{Cu}^{2+}/\text{Cu}}^0$ - anodic peak potential of pure copper (−0.27 V);

$E_{\text{Cu}^{2+}/\text{Cu(Pt)}}^{\text{mix}}$ - anodic peak potential of copper oxidation from Cu-Pt alloys;

\mathcal{E}_{mix} - integral mixing heat of the compounds forming intermetallic phases;

X_{Cu} - mole fraction of Cu.

The mixing heats of alloy formation can be approximately calculated from the energies of formation of covalent bonds between metals using Pauling's correlation equation⁷:

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

where ε_{A-A} , ε_{B-B} - energies of formation of metallic bonds between A and B atoms, respectively;
 χ_A , χ_B - electronegativities of the alloy components.

The energy of the formation of metallic bonds and the electronegativity values of elements are taken from the published data⁷. The mixing heat of copper and platinum calculated from these data is 191.4 kJmol⁻¹. To calculate the energy of mixing the partial energies of formation of metallic bonds $\varepsilon_{Cu-Cu} = 200.9$ kJmol⁻¹, $\varepsilon_{Pt-Pt} = 164$ kJmol⁻¹ and the electronegativities of metals were used.

With the help of equations (1) and (2) the peak potentials of copper oxidation from the different intermetallic phases can be calculated and these data can be compared with the experimentally obtained data: Table 1 shows the comparison.

Table 1. Comparison of the calculated and experimentally determined values of peak potentials of selective electro-oxidation of copper from IMC containing platinum

Potential of an anodic peak of copper	Composition of IMC			
	Cu ₃ Pt, $X_I=0.75$	CuPt ₇ $X_I=0.125$	CuPt ₃ $X_I=0.25$	CuPt $X_I=0.5$
E_{calc} , V	-0.21	0.516	0.31	-0.01
E_{exp} , V	-0.22	No	No	No

Peak potential of copper oxidation is -0.22 V (fig.1), indicating that the composition of intermetallic phase is Cu₃Pt. This peak is used for determination of platinum ions in the solutions by stripping voltammetry.

4. Conclusion

The results presented here show that it is possible to determine Pt (IV) in solutions by recording the anodic stripping voltammograms of copper oxidation when Cu₃Pt alloy phase is precipitated from the appropriate solutions.

References:

1. Dominova I. G., Kolpakova N. A., Stromberg A. G. Determination of platinum in the presence of mercury film by polarography with accumulation. *Journal of Analytical Chemistry*, 1977; **10**: 1980-1983.
2. Kolpakova N. A., Shifris B. S., Shvec L. A. Determination of platinum group metals and gold by stripping voltammetry. *Zh analit khim.* 1991; **10**: 1910-1913.
3. Ustinova E.M., Gorchakov E.V., Kolpakova N.A. Determination binary electrolytic deposit indium-platinum. *Bulletin of Tomsk Polytechnic University*, **320**: 56-58.
4. Ustinova E. M., Gorchakov E. V., Kolpakova N. A. Anodic stripping determination of Pt (IV) based on the anodic oxidation of In from electrochemically deposited Pt-In alloy phases. *Journal of Solid State Electrochemistry*. 2012; **16**: 2455-2458.
5. Lyakishev N.P. Diagrams of binary metal systems. *Mashinostroenie*: Moscow; 1999.
6. Braynina Kh.Z., Neyman E.Ya. Solid state reaction in electroanalytical chemistry. *Khimiya*: Moscow; 1982.
7. Pauling L, Pauling P. Chemistry. Freeman: San Francisco; 1975.