The electrochemical synthesis and investigation of nanostructured Fe-Pt and Co-Pt systems

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Abstract. By means cyclic and anodic linear sweep/stripping voltammetry methods the electrochemical behavior of bimetallic electrolytic nanoalloys and nanostructured powders Fe–Pt, Co–Pt was investigated in acidic (chloride, sulfate, tartrate) and ammonia buffer media with the glassy carbon electrode. The conditions (supporting electrolytes, concentrations of metal ions, voltammetric parameters) of the electrochemical synthesis and voltammetric characterization of the binary systems were established.

1. Introduction

Unique magnetic performance is typical for nanostructured bimetallic Co-Pt and Fe-Pt systems due to the existence of high-coercivity phases with perpendicular anisotropy (e.g., L₁₀) in their structure. This determines a variety of application fields for such systems as thin film coatings, powders, and core-shell systems. Functional properties of bimetallic systems platinum-transition metal are employed when developing magnetic recording means, microelectromechanical systems, and also agents of directional action in cancer diagnosis and therapy [1, 2]. Furthermore, apparent catalytic properties determine the use of the specified systems in chemical and electrochemical catalysis, and also in developing sensor devices to determine bioactive organic compounds [3-5].

The main problem for the synthesis of Co-Pt and Fe-Pt systems is producing phases free of impurities of metal hydroxides and precursor components. Therefore, the task of developing electrolytic deposition methods that may allow producing pure synthesis products under soft conditions is relevant in this respect. Various structures, such as thin films, powders, nanoparticles, and nanofibers, may be produced via these techniques [6-8]. One of the evident advantages for electrodeposition is an opportunity to investigate the phase and elemental composition of the resulting systems through in situ voltammetric methods after selecting appropriate experimental conditions [8 – 10]. The information regarding electrodeposition conditions for nanostructured Co-Pt and Fe-Pt systems is scarce. The known data presented in literary sources deals with the use of electrolytes containing chloride and sulphate ions, organic additives (for example, sulphamate and citrate ions), and metal electrodes [10–15]. An opportunity to perform the electrochemical characterization of nanostructured Co-Pt and Fe-Pt systems both in the form of electrolytic films and powders has not been previously explored. Due to the above, the objective of this work is the exploration of electrodeposition processes and the search for electrochemical conditions for the nanostructured Co-Pt and Fe-Pt systems characterization.

2. Experimental

The CV and ASLV electrochemical measurements were performed in a three-electrode cell using potentiostat/galvanostat Parstat 4000. The working and counter electrodes were the glassy carbon cylinders (l = 15 mm, d = 2 mm) or the glassy carbon (Sigradur) plate (l = 25 mm, w = 5 mm) and the...
reference electrode – Ag/AgCl in 0.1 M KCl. Before experiment working and counter electrode surfaces were polished down to polishing cloths, etching in 5 M H₂SO₄, thoroughly washed with pure water and transferred to the electrochemical cell. Chemicals used were FeSO₄, Fe₂(SO₄)₃, CoCl₂, H₂PtCl₆, supporting electrolytes: 0.1 M NH₄Cl + 0.1 М NH₄OH (рН 9.8), 0.1 M Na₂SO₄ + HCl (pH 2.0); 0.1 M KCl + HCl (рН 1.7); 0.1 М NaCl; 0.2 М C₆H₆O₆ + 0.2М NaOH; all of analytical grade. All solutions were prepared with double-distilled water. рН measurements were carried out using рН-meter Expert 001.

The electrodeposition of the nanoalloys Fe–Pt, Co–Pt was carried out in the potentiostatic mode from the background electrolytes with various ratios of the metal ions concentrations (1·10⁻⁵ – 1·10⁻³ M) at –1.6 V, time of the deposition was 2 – 10 min. During this process the solution stirred with magnetic stirrer. Anodic oxidation was carried out in the potentiodynamic mode, scan rate – 100 mV/s.

The nanostructured Fe–Pt, Co–Pt powders synthesized according to the procedure of chemical reduction given in [16-18] were preliminary cleaned by water or etching agents and then were immobilized on the surface of the working glassy carbon electrode. The X-ray diffraction (XRD) data were recorded by diffractometer Bruker D8 Advance A25 [18, 19]. The chemical composition of the powders was carried out by the method of inductively coupled plasma optical emission spectrometry (ICP-OES) using an iCAP-6500 DUO spectrometer (USA). The SEM images of the NPs were obtained by a Jeol JSM 6390 390 scanning electron microscope.

3. Result and Discussion

The research on the electrochemical behaviour of platinum, iron, and cobalt has been performed through cyclic (CV) and anodic linear stripping voltammetry (ALSV). Moreover, conditions for the formation of electrolytic deposits of metals and binary systems on a glassy carbon substrate have been experimentally determined. Various electrolytes, such as solutions of potassium chloride and sulphate (рН = 1.5) with additives of an organic complexing agent, i.e. tartaric acid, and also an ammonia buffer solution for cobalt and the cobalt – platinum system were scrutinized considering chemical properties of the metals.

![Figure 1](image-url) Anodic voltammetric curves acquired in different electrolytes, 0.1 M NaOH + H₂Tartr, pH 3, 0.5 M NaCl. c(Fe³⁺), 10⁻⁴ M: 1 – 2 ; 2 – 5; 3 – 10; 4 – 16.

The criterium for efficient cathode deposition is the presence of reproducible oxidation peaks of metals in the anode voltammetric curve and the dependence of the peak value on the ion content of the corresponding metal in the electrolyser. As it is known, cobalt and iron form slightly soluble
hydroxides, which should be considered when an electrolyte is selected. Solubility constants of hydroxides are as follows: Fe(OH)$_2$ – 8·10$^{-16}$, Fe(OH)$_3$ – 6.3·10$^{-38}$, Co(OH)$_2$ – 2·10$^{-16}$ [20].

Hydrogen evolution process occurs in parallel in the cathodic region upon metal electrodeposition. Due to this, there are the local alcalinization of the near-electrode layer and even the formation of cobalt and iron oxide-hydroxide compounds on the electrode surface. These phenomena are especially clearly apparent for iron due to the extremely low solubility constant of Fe(OH)$_3$. In the anodic stage, that results in the appearance of a series of additional peaks in the potential range between +0,2 and +0,7 В (Fig.1).

The peaks correspond to iron oxidation processes to yield iron (II) oxide-hydroxide phases followed by transformation of the latter to iron (III) oxide or iron (III) oxo-hydroxide [21]. There is a qualitatively similar oxidation pattern after cobalt deposition. Parameters of these electropositive peaks and the fact itself of their formation allow determining the degree of purity of the resulting metal deposit and, on the other side, identifying the oxide-hydroxide phases by their response in the anodic process upon voltammetric research of nanostructured powders.

As determined by means of ASLV and CV the electrodeposition process of nanostructured iron deposits free of impurities of oxygeneous compounds proceeds in the electrolytes listed in Table 1, except for tartrate. As can be seen, by varying the nature of the background electrolyte and pH, one may change the potential range for iron oxidation by a value between 30 and 120 mV, which is crucial upon the phase analysis via the voltammetric method. Herewith, there have been acquired linear relationships of current peaks vs iron ion concentration in all media, except for 0.1 М KCl + HCl.

| Background electrolyte, ion | pH | $E_{\text{peak}}$, mV | Linearity formula, $c\cdot10^2$ mol/L | Range $c$(M$^{n+}$), 10$^4$ mol/L |
|-----------------------------|----|---------------------|--------------------------------------|---------------------------------|
| 0.1 М KCl + HCl, Fe$^{3+}$ | 1.7 | -430 | – | 2.6 – 9.3 |
| 0.1 М Na$_2$SO$_4$ + HCl, Fe$^{3+}$ | 2.0 | -480 | I = 0.39c + 1.4 | 1.7 – 16 |
| 0.5 М NaCl, Fe$^{3+}$ | 5.5 | -405 | I = 1.48c – 4.1 | 13 – 33 |
| 0.2 М C$_4$H$_6$O$_6$ + 0.2M NaOH, Fe$^{3+}$ | 3.1 | -530$^a$ | I = 0.35c + 2.0 | 1.7 – 16 |
| 0.5 М NaCl, Fe$^{2+}$ | 5.5 | -405 | I = 0.92c + 3.0 | 1.1 – 6.7 |
| 0.1 М KCl + HCl, Co$^{3+}$ | 1.7 | -150 | I = 0.95c + 28 | 0.02 – 3 |
| 0.1 М NH$_4$Cl+NH$_4$OH, Co$^{3+}$ | 9.8 | -450 | I = 2.90c – 4.0 | 2 – 30 |

*Parameters are presented for the peak of iron oxidation.

Electrodeposition of binary systems was carried out in a mode of the preliminary modification of the electrode surface with adatoms of a less precious component. The technique is considered in detail in [9, 10]. Experiments were carried out at various concentrations of iron (II/III), or cobalt (II) ions
and chloroplatinic acid. As can be seen in voltammograms shown in Fig. 2 for electrolyte 0.1 M Na$_2$SO$_4$ + HCl (pH 2.0), upon the co-deposition of iron and platinum, the rate of iron deposition is sharply reduced and, as a consequence, the anodic peak current of iron is decreased; in the region $E_{an} = -190$ mV, the hydrogen desorption peak appears from the electrolytic platinum surface. Herewith, there is the corresponding peak of hydrogen sorption at a potential of $-520$ mV on the cathodic branch. There is no anodic oxidation of platinum under experimental conditions, however, the presence of electrolytic platinum is indirectly proven by hydrogen sorption/desorption peaks. There are similar regularities for all acidic electrolytes explored.

![Figure 2](image)

**Figure 2.** Anodic voltammetric curves for iron and iron-platinum system in 0.1 M Na$_2$SO$_4$ + HCl, c(Fe$^{3+}$), 10$^{-4}$ M: 1 – 7; c([PtCl$_6$]$^{2-}$), 10$^{-7}$ M: 2 – 4; 3 – 8; 4 – 28; 5 – 68.

As determined using quantity of electricity for the cathodic/anodic peaks, at least a hundredfold excess of iron (II/III) ions over chloroplatinate species is required to deposit binary iron-platinum phases. In this concentration region a subsequent increase in chloroplatinate ion content results in a shift of iron anodic peak in the positive direction. That is explained by the more energy consumption which requires for iron selective oxidation from the binary Fe-Pt alloy.

Electrode processes for the iron-platinum system can be presented by the following scheme:

**Cathodic deposition**

- Fe$^{3+} + 3e^- \rightarrow$ Fe
- Fe$^{3+} + [PtCl$_6$]$^{2-} + 7e^- \rightarrow$ Fe$_x$Pt$_y$ + 6Cl$^-$
- [PtCl$_6$]$^{2-} + 4e^- \rightarrow$ Pt + 6Cl$^-$

**Hydrogen adsorption peak:**

- Pt + H$^+$ + e$^- \rightarrow$ Pt(H$_{ads}$)

**Anodic oxidation**

**Iron oxidation peak:**

- Fe $\rightarrow$ Fe$^{3+} + 3e^-$

**Hydrogen desorption peak:**

- Pt(H$_{ads}$) $\rightarrow$ Pt + H$^+$ + e

As demonstrated by scanning electron microscopical investigations of iron-platinum nanostructured alloys deposited on glassy carbon plates from a chloride electrolyte (Figure 3), this system is characterized by island-type growth. Moreover, areas with dendritic and fibrous structure are formed. Cyclic voltammetry data show, the resulting nanoalloys have an average formula of Fe$_{20}$Pt$_{80}$. However, there is no iron in the samples according to the EDX, therefore its shielding with platinum metal occurs, which is explained by the lateral growth of the deposit. The observed features
of the morphology of the nanostructured deposit are due to the hydrogen evolution process in parallel. As a consequence, the electrode surface is partially blocked and the rate of the reduction process of metal ions is decreased.

Figure 3. SEM images for the nanostructured Fe-Pt alloy on glassy carbon surface. Electrodeposition in 0.1 M KCl + HCl electrolyte; \(c([\text{PtCl}_6]^{2-}) = 5.7 \cdot 10^{-5} \text{ M} \); \(c(\text{Fe}^{2+}) = 7.7 \cdot 10^{-3} \text{ M}\).

Conditions that allow eliminating the effect of processes of catalytic hydrogen evolution in the presence of platinum have been determined for the binary cobalt-platinum system. An opportunity for the electrolytic synthesis of Co-Pt thin films in an ammonia buffer electrolyte has been demonstrated through stripping and cyclic voltammetry. It is possible to explicitly trace for a change in the cobalt content in the alloy under these conditions when varying deposition conditions, as there is an oxidation peak for this metal in voltammetric curves upon any platinum content. As can be seen in Fig. 2, the combined progression of reduction processes for ammonia complexes of cobalt and chloroplatinate ions in general leads to a reduction in the cobalt deposition rate. However, it has been noted for small Co\(^{2+}\) ion concentrations (till \(10^{-5} \text{ mol/L}\)) the electrodeposition of platinum leads to some increase in cobalt current apparently due to at the initial step due to facilitating the nucleation process (Fig. 4).

Figure 4. Cobalt peak current vs chloroplatinate ion concentration in the cobalt-platinum binary system. \(c(\text{Co}^{2+}) = 2 \cdot 10^{-4} \text{ M}; 0,1 \text{ M } \text{NH}_4\text{OH} + 0,1 \text{ M } \text{NH}_4\text{Cl}\).

As illustrated by research performed in the ammonia buffer medium, there is a shift of the cobalt peak towards more positive potentials in the presence of platinum due to the formation of the nanostructured cobalt-platinum alloy on the electrode surface (Figure 5 b). The existence of solid solutions and intermetallic compounds (IMC), such as CoPt and CoPt\(_3\), recorded for micro-alloys and
appropriate nanostructured powders [16, 21] is likely in the case considered. However, IMC phases do not show themselves voltammetrically under experimental conditions.

There are no hydrogen adsorption/desorption peaks in the ammonia buffer, therefore in order to assess the platinum content in the nanostructured system, a method for transferring the electrode into an acid chloride electrolyte has been envisaged. The main experimental steps involve selective cobalt oxidation in the platinum alloy in the course of potential cycling and chemical etching in an HCl solution. Afterwards, the platinum electrode is placed in a chloride electrolyte of a certain acidity and a series of CV curves are recorded until the stabilization of adsorption/desorption peaks in the cathodic and anodic stages of the process. As determined, the optimum parameters for these peaks may be recorded in an electrolyte pH range of 2.2–2.8.

**Figure 5.** CV curves for cobalt–platinum system in ammonia buffer (A) and chloride (B) medium; A - \( c(Co^{2+}) = 7 \cdot 10^{-5} \text{ M} \) (1), \( c(PtCl}_6^{2-}) \), \( 10^{-6} \text{ M} \): 0.4 (2); 1 (3); 7(4); B – \( c(PtCl}_6^{2-}) = 2.3 \cdot 10^{-5} \text{ M} \) (1); \( c(Co^{2+})\), \( 10^{-4} \text{ M} \): 3.1 (2), 6.4 (3). Anodic branch on the top.

In chloride medium (0.1 M KCl + HCl), as with the phenomena observed in the iron-platinum system, voltammograms are complicated with hydrogen adsorption/desorption peaks (Fig.5 B). Furthermore, phase cobalt peak becomes apparent upon a significant excess (in more than 50 times) of cobalt ions over chloroplatinate ones in the electrolyser. Hence, there is also a significant decrease in a deposition rate of cobalt in the presence of platinum in this instance.

The performed experiments have formed the basis for developing the voltammetric technique of the electrochemical response investigations of nanostructured Fe-Pt powders and suspensions specifically attached to the surface of glassy carbon. The fundamental concept of the technique is the sequential performance of the steps of gradient anodic oxidation and cathodic reduction in the mode of stripping and cyclic voltammetry. As a consequence, metal and oxide-hydroxide phase peaks are recorded in the anode process and those of metals in the form of oxides and hydroxides. The latter peaks are registered after cathode reduction. Figure 6 reports cyclic voltammetry curves for samples of Fe-Pt of diverse spatial arrangement.

Hydrogen adsorption/desorption peaks are recorded in a potential range of \(-0.5 \div -0.2 \text{ V}\). They indicate the presence of the phase of pure platinum or platinum in the binary Fe-Pt phase (it is impossible to differentiate these phases at this step of research) and a series of oxygen-containing iron compounds formed upon chemical synthesis and storage of the samples (a potential range of + 0.3 \div +0.6 \text{ V} in the anodic scan). Current peaks correlate with absolute metal concentrations; there is no changing potentials and the total picture of oxidation/reduction when varying an Fe/Pt ratio. The appearance of the anodic iron peak after carrying out the electrodeposition step indicates that iron in the sample is found as a part of the binary phase.
Figure 6. Cyclic voltammograms for the nanostructured powders (A) and suspension (B) Fe-Pt attached to glassy carbon, 0.1 M KCl + HCl. Anodic branch on the top.

Electrochemical research outcomes are in agreement with XRD data regarding the phase composition of nanostructured powders and atomic emission analysis results. The phase is comprised of solid solutions of varying composition and its content indicates the correspondence of metal concentrations to the formula determined upon synthesis [16]. Thus, the voltammetric method may be used to explore nanostructured bimetallic systems, in particular, to analyse the elemental composition of the phases, and also their purity extent. 

4. Conclusion
The electrochemical response of nanostructured bimetallic systems Fe–Pt and Co–Pt by means voltammetric methods (CV and ASLV) can be used in the investigation of their physico-chemical characteristics such as phase and elemental composition, spatial phase arrangement, stability to the oxidation, etc. It is worth indicating that the electrolytic synthesis of nanostructured iron-platinum systems free of oxo-hydroxide inclusions is likely over glass-carbon substrates when using acid chloride, sulphate media with pH ≤ 2, whereas cobalt-platinum – acid chloride and ammonia buffer media. In order to perform the voltammetric research on nanostructured Me-Pt systems, it is required to consider catalytic activities of the specified metals in hydrogen emission processes and an opportunity to form oxygen-containing analogues by virtue of changing the pH of the medium.

Acknowledgments
The authors like to thank Sozinov S.A. for the assistance with SEM analysis.

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