Electrochemical Response of Nanostructured Iron-Platinum Systems Produced by Potentiostatic Deposition

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Abstract

The paper presents the results of a voltammetric study of electrodeposition and electrooxidation of nanostructured systems based on iron and platinum with glassy carbon electrodes in various electrolytes. The capabilities of anodic and cyclic voltammetry in the characterization of nanometallic deposits were shown. The conditions for electrochemical synthesis and voltammetric studies of nanostructured electrolytic iron-platinum systems were established.

Key words: binary systems, iron, platinum, voltammetry, electrodeposition, anodic oxidation

INTRODUCTION

Making polymetallic nanoscale and nanostructured systems with specified properties and developing methods of analysis of their composition and structural features is a promising trend of modern material sciences. Film nanostructures based on iron and platinum that are the most demanded materials to develop magnetic carriers of ultra-high density are of special interest due to their coercivity that is the record for bimetallic systems. High temperatures of blocking the supermagnetic condition also determine a large capacity of the use of bimetallic Fe–Pt nanoparticles in many areas of medical science including cancer therapy. Furthermore, these systems are used when making catalysts for electrochemical processes and sensor devices to determine bioactive compounds [1–5].

There are various physical methods for the preparation of metallic film structures, including vacuum deposition, magnetron deposition, laser sputtering, *etc.*; however, all of them require expensive equipment. Alternative synthesis methods for nanometallic films are electrochemical ones, *e.g.* various options of electrodeposition characterised by a number of advantages, such as implementation simplicity, economic accessibility, an opportunity to regulate the composition of a film, the thickness of the latter, and by a high degree of the purity of synthesis products. In addition, electrochemical methods, such as voltammetry, allow investigating characteristics of nanometallic systems directly during their preparation [6]. The electrodeposition method in relation to the iron–platinum system has been poorly developed. For example, the authors of papers [7–10] used synthesis options based on simple chloride and sulphate electrolytes, more rarely, those containing strong complexing agents [11–13]. Currently, there are no approaches towards the voltammetric investigation of phase compositions of such systems, components of which are significantly different according to redox potentials, and also have catalytic activities in processes of electrochemical evolution of hydrogen and a trend to form hydroxides.

The objective of the research work was to determine conditions for electrolytic deposition of nanostructured iron−platinum systems. In order to accomplish this task, the electrochemical behaviour of iron and platinum individually and as a component of a binary system was investigated in various background electrolytes by stripping voltammetry and cyclic voltammetry.

EXPERIMENTAL

Electrodeposition and electrooxidation processes of thin film iron−platinum structures were investigated through cyclic voltammetry (CV) and stripping voltammetry (SV) using Parstat 4000 and Versastat 3 potentiostat/galvanostats in the three-electrode mode. Glassy carbon electrodes acted as working and counter ones; a silver chloride electrode in a 0.1 M KCl solution was the reference one. The electrolysis process was carried out at a potential of 1.6 V, metal electrodissolution − at a linearly varying potential ($v = 100$ mV/s).

In order to prepare solutions, bidistilled water, and also highly pure and chemically pure reagents were used. Compositions of deposition electrolytes are the following: sulphate − 0.1 M Na_2SO_4 + + H_2SO_4 (pH 2.0); chloride − 0.1 M KCl + H_2SO_4, pH 3.0; ammonia tartrate − 0.1 M $C_4H_6O_6$ + 0.1 M NH_4OH (pH 7.1); tartrate buffer − 0.02 M $KHC_4H_4O_6$ (pH 3.7); chloride-tartrate − 0.06 M KCl + 0.08 M $C_4H_4O_6$ (pH 2.1) with additives of $Fe(NO_3)_3$ and H_2PtCl_6 solutions. The pH value was measured using an Ecotest 2000 pH meter/ionometer.

RESULTS AND DISCUSSION

Electrochemical behaviour of iron

Electrodeposition processes of iron subgroup metals in aqueous solutions are significantly complicated by the formation of oxide-hydroxide species due to local alkalizing a near-electrode

layer even at low pH values of the electrolyte [14]. In turn, platinum electrodeposition is accompanied with hydrogen catalytic evolution processes that flow in parallel, therefore it is required to use less acid media. Thus, selecting the optimum background electrolyte to produce and characterize the Fe−Pt system is a complex task.

Considering data regarding chemical properties of iron and platinum, in particular, those about an opportunity to form complex ions and pH ranges that ensure the absence of hydroxides, both simple sulphate and chloride media with various pH values, and also solutions with additives of tartaric, citric, and salicylic acids, and well as ammonia as complexing agents were considered as background electrolytes. As shown, iron electrodeposition proceeds efficiently in all electrolytes (Table 1), which is proven by the formation of the anodic peak in voltammetric curves that corresponds to metal oxidation from the electrode surface (Fig. 1). Alongside with that, as demonstrated by experiments, the oxidation peak of iron in sulphate and chloride electrolytes is recorded in the same potential range as the platinum analytical signal. In order to change the iron peak position, complexing agents were added into the electrolyte.

Introducing additives of citric and salicylic acids facilitates reducing the iron peak probably due to the formation of stable complexes, therefore the specified electrolytes are not suitable in the used concentration range.

Tartaric acid and its salts may be used as a complexing additive, however, even in the presence of a significant excess of a complexing ion, the pH value of the deposition solution should not be higher than 2.5. As can be seen in Fig. 1, *b*, when the pH value is increased (≥3), the iron peak is distorted and wide maxima are formed, the latter corresponding to oxidation processes of oxohydroxide phases.

Table 1 presents generalized data regarding parameters of the anodic peak of iron in various

TABLE 1

Parameters of the anodic peak of iron in various background electrolytes

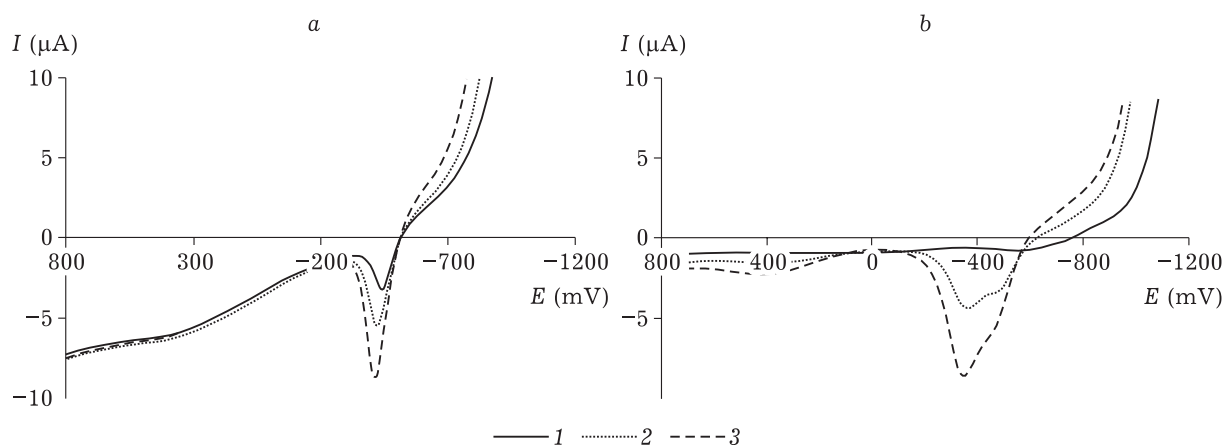| Background electrolyte	E_{peak}, mV	Equation relationship $I_{peak} = f(c)$, s · 10^4, mol/L	Range of (Fe^{3+}), 10^{-4} mol/L
0.1 M Na_2SO_4, pH 2.0	−470	I = 13c − 1.4	0.2−1.2
0.1 M KCl, pH 1.5	−405	I = 2.2c − 0.5	0.3−3.2
0.02 M $KHC_4H_4O_6$, pH 3.7	−500	I = 12c + 0.8	0.2−3.5
	−360		
0.06 M KCl + 0.08 M $C_4H_6O_6$, pH 2.1	−410	I = 2.4c + 0.6	0.1−1.0
0.1 M $C_4H_6O_6$ + 0.1 M NH_4OH, pH 7.1	−500	−	1.6−8.3
	−360		

Fig. 1. Anodic voltammetric curves of iron oxidation in 0.06 M KCl + 0.08 $C_4H_6O_6$, pH 2.1 (*a*) (concentration, $c(Fe^{3+})$, 10^{-4} M: 1.6 (*1*), 2.2 (*2*), and 3.5 (*3*) and in ammonium tartrate solution, pH 7.1 (*b*) ($c(Fe^{3+})$, 10^{-4} M: 1.7 (*1*), 4.9 (*2*), and 8.1 (*3*).

electrolytes. As can be seen, the variation of the type of the background electrolyte and pH, and also the introduction of complexing additives change the potential range, in which iron oxidation occurs, by a value between 50 and 150 mV. Herewith, linear relationships of current iron peak oxidation *vs* the Fe^{3+} ion concentration in all media, except for the ammonium tartrate one, were yielded.

There are the maximum deposition rates in sulphate and tartrate electrolytes.

Electrochemical behaviour of platinum and the Fe-Pt binary system

Electrodeposition processes of platinum have been extensively explored for many years. An opportunity to use solid electrodes based on carbon materials and electrolytes of various types to produce nanostructured systems based thereon was demonstrated [15]. A typical feature of Pt consists in the fact that its dissolution processes in aqueous electrolytes proceed in the potential range that is more positive than + 1.0 V and are masked by background currents [16−18]. However, the peaks in the voltammetric curve that correspond to hydrogen sorption/desorption processes indirectly indicate the presence of Pt metal or platinum complex ions in the system.

Potentiostatic deposition of platinum was carried out under conditions as indicated above using electrolytes described in Table 1. Hydrogen sorption/desorption peaks (Fig. 2) were recorded by CV for all electrolytes. The former attest to the formation of platinum on the electrode surface (*e.g.*, for 0.1 M H_2SO_4, E_{anod} = −420 mV, E_{cathod} = −560 mV).

The anodic and cathodic peak currents are linearly linked to the concentration of complex plat-

inum chlorides in the electrochemical cell and their value is determined by the electrolyte pH. The presence of complexing additives has a slight effect on the parameters of the indicated peaks.

Adding iron ions to the solution in sulphate and chloride electrolytes results in a minor increase of sorption/desorption peaks (see Fig. 2) and a rise in the anodic current within the −800… −600 mV range, which may be related to the formation of the binary Fe−Pt system. It is not possible to see the iron oxidation peak probably because of this reason, and also due to its matching to the hydrogen desorption peak.

Changing the sequence of introducing metals into the electrolyser leads to the same results: the iron peak is not recorded even in the presence of
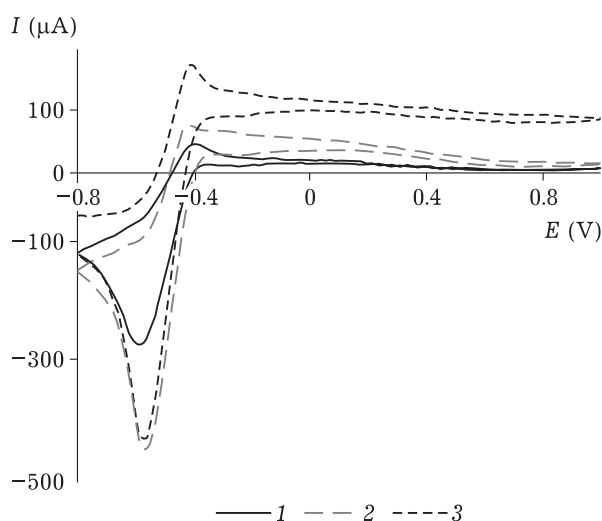

Fig. 2. Cyclic voltammetric curves acquired for nanostructured platinum and the binary Fe-Pt system in 0.1 M Na_2SO_4, pH 2, $c(PtCl_6)^{2-}$, 10^{-5} M: 1 (*1*), 3 (*2*), and 3 (*3*) + $c(Fe^{3+})$ = $5 \cdot 10^{-5}$ M. Anodic semicycle is on top. For display purposes, voltammetric curve 3 is shifted along the current axis by 70 μA.
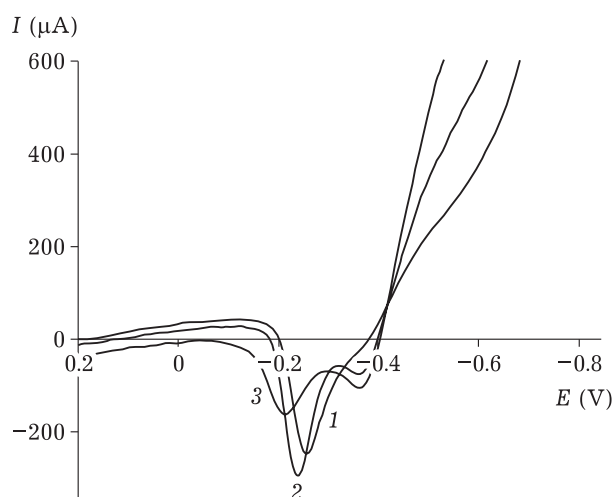
Fig. 3. Anodic branches of cyclic voltammetric curves for nanostructured Fe−Pt systems acquired using 0.1 M KCl + 0.2 M $C_4H_6O_6$. Ion content, $c(Fe^{3+}) = 1 \cdot 10^{-3}$ M; $c(PtCl_6^{2-})$, 10^{-5} M: 1.3 (*1*), 2.0 (*2*), and 3.3 (*3*).

Fig. 4. Anodic voltammetric curves for nanostructured iron-platinum systems in ammonium tartrate buffer solution, pH 7.1 $c(Fe^{3+}) = 8 \cdot 10^{-4}$ M, $c(PtCl_6)^{2-}$, 10^{-5} M: 0 (*1*), 0.1 (*2*), 0.2 (*3*), and 0.5 (*4*).

very small amounts of platinum on the electrode surface. The overlapping of iron and platinum signals and the negative effect of hydrogen catalytic isolation processes prevents the unambiguous interpretation of data regarding changing peak parameters upon joint deposition and, accordingly, the phase composition of the iron–platinum alloy. In order to produce correct conclusions regarding the degree of the mutual effect of components upon electrodeposition and phase composition change when varying deposition conditions, it is required to select such a composition of the electrolyte that would allow recording oxidation peaks in various potential ranges. For this reason, solutions with tartaric acid additives were used later on.

As can be seen from Fig. 3 data acquired for the electrolyte, 0.1 M KCl + 0.2 M $C_4H_6O_6$ pH 1.5, the iron peak is decreased when adding chloroplatinate to the electrochemical cell and the hydrogen desorption peak appears in the region $E_{anod} = -390$ mV. At the same time, the corresponding hydrogen sorption peak is recorded in the cathodic branch at a potential of -580 mV. A subsequent increase in the content of chloroplatinate ions leads to shifting the iron oxidation peak (from about −270 to −215 mV), which indicates the formation of the Fe−Pt binary alloy with varying composition [6, 19].

It was possible to track decreasing the iron peak ($c(Fe^{3+}) = 8 \cdot 10^{-4}$ M) related to the metal inclusion into the alloy in an ammonium tartrate electrolyte with a pH of 7.1 upon the subsequent addition of chloroplatinate ion additives. Nevertheless, there was a parallel increase in the des-
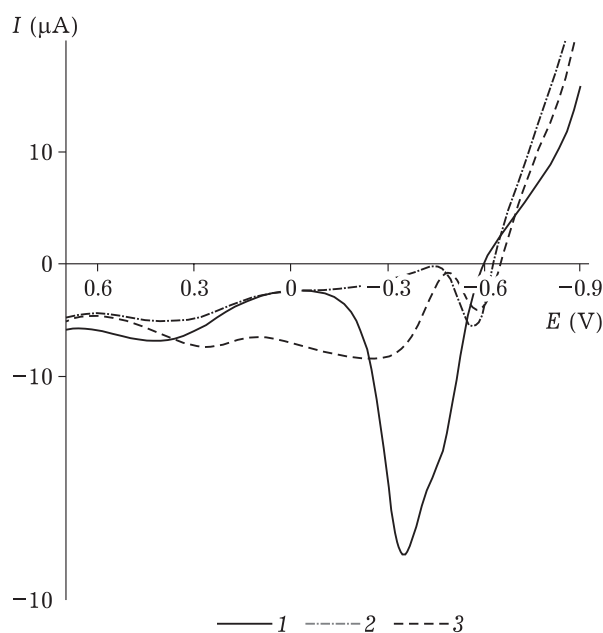
orption peak and in a broad spike corresponding to oxidation of oxide-hydoxide compounds in the 200−600 mV range (Fig. 4).

CONCLUSION

Thus, the electrolytic preparation of nanostructured iron-platinum systems that are free of oxohydroxide inclusions is possible over glassy carbon substrates when using acid, chloride, sulphate, and tartrate media with pH ≤ 2.5. In order to perform the voltammetric investigation of these systems, the catalytic activity of the specified metals in hydrogen evolution processes and an opportunity to form undesirable compounds upon changing the pH should be considered. Varying electrolyte composition, in this case, due to introducing tartaric acid additives based on potassium chloride has made it possible to separate analytical signals of platinum and iron, and also to obtain the proof of Fe−Pt alloy formation upon metal cathodic deposition. This technique opens up opportunities for the electrochemical investigation of chemical and phase compositions of the nanostructured iron-platinum system.

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