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Two-step fabrication of iron-containing polyaniline composites for electrocatalytic hydrogenation of nitroarenes

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ABSTRACT

Polyaniline + Fe + FeO + Fe_3O_4 composites were prepared as powder by a two-step process: (1) introduction of FeO into oxidative polymerization of aniline and (2) electrochemical reduction of the powder deposited on a Cu cathode in aqueous NaOH. The structure and morphological features were studied by atomic emission spectroscopy, X-ray diffraction analysis and electron microscopy. The polyaniline–iron composites were used in electrohydrogenation of *p*-nitrobenzoic acid (*p*-NBA). Their electrocatalytic activity in the process is due to the formation of iron particles as a result of the electrochemical reduction of Fe^{2+} cations in FeO. The electrocatalytic activity is clearly demonstrated by the electrocatalytic hydrogenolysis of the intermediate hydroxylaminobenzoate to the aminobenzoate. Magnetic properties have been determined for the composite with optimal FeO content before and after the electrocatalytic hydrogenation of *p*-NBA.

1. Introduction

The introduction of metal-containing inorganic compounds in the form of oxides, hydroxides, metal salts and their nanoparticles into polymer matrices makes it possible to obtain new composite materials possessing specific physicochemical properties (optical, electrically conductive, magnetic, catalytic, etc.) [1,2]. Polyaniline (PAni) is one of the most promising electrically conductive polymers due to the simplicity of preparation, low cost of the initial monomer and the ability to change its physicochemical properties depending on the acidity of the medium, the degree of oxidation of the polymer backbone and the particle morphology [3]. Close attention is paid to iron-containing PAni composites due to the possibility of creating materials with unique magnetic and conductive properties [1,4–13]. The usual subjects of research are metal–polymer composites with Fe_3O_4 and Fe_2O_3 iron oxides.

In our studies of polyaniline–metal composites [14,15], it was established that the introduction of the metal salt into the polymer by chemical methods followed by the use of the resulting composites to activate a cathode in the electrochemical reduction of organic compounds is accompanied by the formation of metal particles in the zero-valence state. However, cathodic activation by PAni composites with the introduced iron (II, III) salt does not lead to the reduction of its cations, and the formation of composites with Fe^0-particles.

In this work, PAni + Fe^0 + FeO + Fe_3O_4 composites were prepared by incorporating the FeO (wüstite) powder sonicated into oxidative polymerization of aniline and subsequent reduction in an electrochemical cell. The electrocatalytic activity of the resulting iron-containing composites toward the electrocatalytic hydrogenation of *p*-nitrobenzoic acid (*p*-NBA) has been studied. The hydrogenation product, *p*-aminobenzoic acid, is of great practical importance, as it belongs to the vitamins of group B and is a precursor in the synthesis of folic acid, as well as participating in various other organic syntheses. It should be noted that iron-containing composites without PAni (Fe + FeO + Fe_3O_4), according to [16], exhibit stable and high electrochemical characteristics when used as an anode material in lithium-ion batteries.

2. Experimental

Iron-containing PAni composites were obtained by introducing the FeO iron oxide into the reaction medium of oxidative polymerization of aniline (ammonium persulfate was used as an oxidizer). The ratios of aniline/FeO were 1:0.2, 1:0.4, 1:0.6, 1:0.8, 1:1 and 1:1.5. The iron oxide was pre-treated with ultrasound in distilled water for 20 min. It was then introduced into the reaction mixture after its pH had been raised to 8 by an addition of 1 M NH_4OH solution. The resulting mixture was left for 24 h. The precipitate was filtered off and washed with

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Table 1
Electrocatalytic hydrogenation of *p*-NBA on PAni + FeO composites.

Entry	Composites	Iron content in 1 g of composite, g	*W*, mL H_2/min (α = 0.25)	*η*, % (α = 0.25)	*α*, %	$Q_I + Q_{II}$, A·min	Current efficiency for stage II, %
1	Cu cathode	–	3.7	34.6	70.1	30 + 225	13.92
2	Pb cathode	–	6.2	60.3	80.2	75 + 127	28.21
3	PAni + FeO (1:0,2)	0.134	4.6	41.4	67.4	45 + 135	22.30
4	PAni + FeO (1:0,4)	0.284	4.3	38.0	73.1	45 + 165	19.79
5	PAni + FeO (1:0,6)	0.291	6.4	47.0	96.0	45 + 135	31.76
6	PAni + FeO (1:0,8)	0.326	5.6	54.2	82.8	60 + 150	24.66
7	PAni + FeO (1:1)	0.410	6.0	52.2	87.4	52 + 150	26.03
8	PAni + FeO (1:1) - 2 (Cu)	0.404	7.2	70.8	92.7	60 + 150	27.61
9	PAni + FeO (1:1) - 2 (Pb)	0.404	7.7	77.5	83.6	75 + 135	27.66
10	PAni + FeO (1:1,5)	0.486	3.6	30.4	90.3	30 + 165	24.45

distilled water, then with acetone, and dried at 80 °C. The PAni + FeO (1:1) - 2 composite was re-synthesized later for a comparison of the results of the electrohydrogenation of *p*-NBA on the Cu and Pb cathodes. Some disagreements with the previously obtained results for Pani + FeO (1:1) composite deposited on a Cu cathode (see the data in Table 1 below) are caused by difficulties in reproducing in the synthesis of these composites all the fine details of the structure of the polymer matrix (polyaniline) and the distribution of dopant particles therein, which affect the properties of the composites.

The iron content (Fe^{2+} and Fe^{3+}) in the filtrates after the synthesis of PAni composites was determined by atomic emission spectroscopy; the iron content in the resulting powdered composites was then calculated using the difference with the initial metal content in the FeO.

The structure and phase constitution of the synthesized PAni + FeO composites were studied by X-ray diffraction (XRD) analysis on DRON-2 diffractometer. Their morphological features were investigated using a TESCAN MIRA 3 LMU scanning electron microscope.

Experiments on the electrocatalytic hydrogenation of *p*-nitrobenzoic acid were carried out in a diaphragm electrochemical cell with an external magnet under the cathode, as described in [14,15]. The iron-oxides-containing PAni composite (weighing 1 g) was deposited on a horizontally placed copper cathode and for comparison on a lead cathode. The current density was 1.19 kA/m^2 (I = 1.5 A, the area of the visible cathode surface is 0.126 dm^2), the temperature 30 °C. The 75 mL of 2% NaOH solution was used as a catholyte (an anolyte – 60 mL of 20% NaOH solution). At first, the PAni + FeO composites were saturated with hydrogen, until the ratio of gases evolved $V(H_2):V(O_2) = 2:1$ was established. Then, the organic compound (0.774 g of *p*-NBA) was injected into the cell. The average rate of the hydrogenation reaction (*W*), hydrogen utilization coefficient (*η*) and conversion of *p*-NBA (*α*) were calculated by the following relations: $W = \Delta V_t / \Delta t$ (the average rate was determined from these data up to α = 25%); $\eta = [(2\,V(O_2) - V(H_2)] / 2\,V(O_2)] \cdot 100\%$ at the value of $\alpha = 25\%$, and $\alpha = V_t / V_{theor.} \cdot 100\%$, where V_t is a volume of absorbed hydrogen at the reaction time *t* determined using the volumes of gases evolved $V_t = k(2\,V(O_2) - V(H_2))$ (*k* is a barometric coefficient); $V_{theor.}$ is the calculated volume of hydrogen for complete hydrogenation of the nitro group in the starting amount of *p*-NBA.

The magnetic characteristics of PAni composite with an aniline/FeO ratio of 1:0.6 before (*1*) and after (*2*) electrocatalytic hydrogenation of *p*-NBA were determined by the vibration method on the automated system Cryogenic VSM CFS-9T-CVTI. The measurements were performed at a temperature of 300 K in the magnetic field range up to 40 kOe.

3. Results and discussion

Oxidative polymerization of aniline in a hydrochloric acid medium using ammonium persulfate was discussed in detail in [17]. As a result, polyaniline is obtained in the form of its hydrochloride salt (emeraldine salt) which is a dark green color. In this work, iron oxide FeO was incorporated into the polymerization reaction medium after adjusting its pH to 8, therefore polyaniline in all the synthesized composites has the shape of the emeraldine base, which has low electrical conductivity properties.

The phase constitution of synthesized PAni + FeO composites with different aniline/FeO ratios before and after their use as catalysts in the electrohydrogenation of *p*-NBA was studied by means of XRD analysis. As an example, the X-ray diffraction patterns of PAni + FeO (1:1) - 2 composite are shown in Fig. 1.

It can be seen from the diffraction patterns that the phase constitution of the composite before electrohydrogenation (Fig. 1, *a*) contains the crystalline phases of the introduced wüstite (FeO) and magnetite (Fe_3O_4) in addition to the amorphous phase of the polymer. The intensity of the peaks corresponding to wüstite in the diffraction patterns of all composites is higher than the intensity of magnetite peaks, which indicates a higher content of FeO compared with Fe_3O_4. It should be noted that the initial FeO powder also contains magnetite in a smaller amount than wüstite. In the X-ray diffraction pattern of the composite, there is also one weak peak with an interplanar distance *d* = 2.70 Å relating to hematite (α-Fe_2O_3). That means that Fe_2O_3 oxide is present in small amounts in the phase constitution of PAni + FeO composites.

It can be seen from the XRD pattern of PAni + FeO (1:1) - 2 composite after the hydrogen saturation stage (Fig. 1, *b*) that already at this stage, crystalline phases of iron in the zero-valence state appear in the composite as a result of the electrochemical reduction of Fe^{2+} cations in FeO. This is confirmed by a decrease in the intensity of the iron oxide peaks. We can also note a certain relative decrease in the intensity of the peak at *d* = 2.53 Å, which belongs to magnetite. However, verification experiments with Fe_3O_4 powder deposited on a Cu cathode did not reveal its ability to effect the electrochemical reduction under the same conditions described in the Experimental section.

The XRD pattern of PAni + FeO (1:1) - 2 composite deposited on a Cu cathode after electrocatalytic hydrogenation of *p*-NBA (Fig. 1, *c*) is almost the same as the XRD pattern for the composite after the hydrogen saturation stage (Fig. 1, *b*), but with a higher peak for Fe^0 relatively to the FeO peak. Fe^0 crystalline phases with their distinctive peaks in the XRD patterns are present in all the composites after the hydrogenation process. However, there is no correlation between the increase in the amount of FeO introduced and the increase of metallic iron (Fig. 2, *a–d*).

The PAni + FeO (1:0,6) and PAni + FeO (1:1) composites show the highest content of reduced iron, according to the intensity of the peaks in their XRD patterns (Fig. 2, *a* and *c*). An increase in the amount of iron (II) oxide introduced into the polymer to an aniline ratio of 1:1.5 leads to the formation of crystalline phases of zero-valence iron with peaks of much lower intensity (Fig. 2, *d*). Because it is the Fe^0 metal particles that catalyze the hydrogenation of the nitro-aromatic compound under investigation, the electrocatalytic activity of the synthesized composites should depend on Fe^0 content.

According to the XRD pattern of PAni + FeO (1:1) - 2 composite deposited on a Pb cathode after electrocatalytic hydrogenation of