Electrochemical Properties of Rhodium- and Gold-Containing Polyaniline Films

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Abstract—Graphite-supported polyaniline films (PANI) containing rhodium particles were obtained by two procedures: metal electrodeposition on a prepared PANI film and electropolymerization. The adsorption/desorption and electrowinning of hydrogen on these films were observed for both types of synthesized composite films. PANI/Au composites were synthesized using the PANI films deposited onto a gold electrode. High anode potentials were further applied to the electrode in the presence of chloride ions, leading to a dissolution of gold and its transfer to the films during subsequent electroreduction. The amounts of the chloride complexes of gold formed in this procedure were determined by cyclic voltammetry of their electroreduction.

Keywords: polyaniline, modified electrodes, cyclic voltammetry, composite materials

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1. INTRODUCTION

The group of electroactive polymers studied during the last 30 years includes polymers based on polyanilines, polypyrroles, and polythiophenes [1, 2]. The organic conducting polymer polyaniline (PANI) is often used as a material of this kind to modify the properties of the electrode surface. Interest in it arises from the high stability of the electrochemical response of films and its good electric and optical properties, which have found wide use in practice.

PANI films have a number of advantages, including easy and fast methods for polymer deposition, the possibility of synthesizing them from aqueous solutions of electrolytes, and stability. The three-dimensional porous structure of the polymer allows the use of PANI as a conducting matrix for including metal particles from solutions of their salts and creating new composite materials on this basis [3–9]. The resulting metal clusters are stabilized in the polymer due to their interactions with nitrogen-containing groups.

The majority of studies were devoted to the investigation of the possibility of incorporating metal particles in the polymer films and qualitative structural and morphological characterization of the composites formed. Many studies dealt with the introduction of palladium in PANI films [3–8].

2. EXPERIMENTAL

Polyaniline films were synthesized in a three-electrode cell by electropolymerization of the aniline monomer by cycling the potential in different ranges. All potentials are given relative to the silver chloride electrode in a saturated KCl solution. The upper bound of the potential was chosen such that it provided effective oxidation of aniline. As a result of preliminary experiments, it was chosen to be 0.9 V. The lower bound was 0 V. Synthesis was performed in a solution containing 1 M HNO3 and 0.1 M aniline at a potential scan rate of 20 mV/s generally in 10 cycles. The estimated thickness of the resulting films (10 synthesis cycles) was 0.4–0.5 μm. It was found that oxygen did not affect the experimental data and experiments, therefore, were conducted without preliminary deaeration of the working solutions. All electrochemical studies were conducted with freshly synthesized films at room temperature. The cell was washed with distilled water. Aniline was distilled before the synthesis.

The PANI/Rh composite films were synthesized by two methods:

(1) Simultaneous deposition of polyaniline and rhodium during cycling from solutions containing 1 M HNO3, 0.1 M aniline, and Na3RhCl6 in different concentrations (2 × 10–3, 4 × 10–3, and 8 × 10–3 M). The reduction of rhodium from this solution started at a potential of approximately −0.15 V and the potential thus changed from −0.3 to 0.9 V in most cases. The change in the range of potentials during synthesis did
not effect the film thickness (~0.5 μm in 10 synthesis cycles).

(2) The second procedure was similar to the one described in [3]. The electrode was preliminarily covered with a polyaniline film and rhodium was then deposited onto the film. The electrode with the PANI film was submerged in a solution containing 0.1 M HNO₃, and 8 × 10⁻³ M Na₃RhCl₆ (first procedure) at v = 20 mV s⁻¹: (1) first, (2) third, (3) fifth, (4) seventh, and (5) tenth cycles.

The PANI/Au composite films were obtained by the oxidation of a gold electrode substrate with a preliminarily deposited polyaniline film in chloride-containing solutions by the procedure of [9]. The electrode was kept at a potential of +1.0 V for different periods of time from 0 to 250 s and the gold(III) complexes (the products of oxidation) were then reduced with a polyaniline film and rhodium was then deposited onto the film. The electrode with the PANI film was kept for some time in the synthesis solution.

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The PANI film thickness was evaluated using the density of PANI 1.5 g cm⁻³ [10].

3. RESULTS AND DISCUSSION

3.1. Synthesis of the PANI Film

Polyaniline was deposited by the oxidation of its monomer at a potential of 0.8–0.9 V. The resulting PANI film placed in a supporting electrolyte (1 M HNO₃) gave distinct peaks at 0.1–0.25 V and ~0.8 V on the voltammogram, called below the peaks of the first and second redox transitions of PANI, respectively, and intermediate peaks at 0.45–0.6 V. The latter peaks were attributed to the impurity structures formed during the synthesis, e.g., phenazine heterocycles. They are often attributed to quinol, which can be formed in the hydrolysis of the oxidized form of PANI [2].

The considerable difference between the cathode and anode peak potentials of the first PANI redox system (at 0.1–0.25 V) can be explained by a rearrangement of the structure of PANI during this redox process [2]. At the same time, in our experiments at −0.8 V, the polymer oxidation was almost reversible.

3.2. Deposition of PANI Films Containing Rh Particles by Cyclic Voltammetry

The PANI/Rh system was conveniently prepared by codeposition of polyaniline and rhodium by cycling the potentials in the range suitable for both the oxidation of aniline and the reduction of rhodium complexes. The potential of the GC electrode placed in a solution of 1 M HNO₃, 0.1 M aniline, and Na₃RhCl₆ (taken in different concentrations) was varied from −0.3 to 0.9 V at a rate of 20 mV/s. The recorded curves are shown in Fig. 1 for a rhodium salt concentration of 4 × 10⁻³ M. Synthesis was generally performed in 10 cycles. According to Fig. 1, the PANI peaks (at 0.1–0.25 and −0.8 V) and the cathode currents at −0.2 V and lower negative values increase during the synthesis, which can only be attributed to hydrogen evolution on deposited rhodium. Catalysis of hydrogen evolution by the low-valence rhodium complexes seems unlikely in this case because these complexes cannot be fixed in the PANI film by their complexation with the polymer or electrostatic interaction with it since PANI is in the uncharged reduced form at potentials of the cathode evolution of hydrogen. For the noncomposite PANI film, the cathode evolution of hydrogen is not observed in this range of potentials.

Anode peaks also appeared at −0.15 V during synthesis due to the oxidation of adsorbed hydrogen or intermediate Rh(II). The nature of these peaks will be considered in detail in the course of the discussion of Fig. 2 below.

Figure 2 presents the voltammograms of the product for PANI/Rh systems synthesized from solutions with different concentrations of Na₃RhCl₆ in the supporting electrolyte (1 M HNO₃). The CVA curve of the PANI film without metal inclusions is given for comparison. A certain scatter in the intensity of the peaks of the first redox transition of PANI is explained by