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Metal-containing Polymer Coatings Based on Poly(2-aminothiazole)

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Abstract—Polymer film based on 2-aminothiazole has been prepared at the surface of glassy carbon electrode via electropolymerization. The film has been modified via electrodeposition of rhodium particles. Hydrogen reduction has been observed at the so prepared composite films. Rhodium nanoparticles have been found uniformly distributed within the polymer matrix. Amount of the deposited metal depends on time of the electrode keeping in the rhodium salt solution. The prepared composite metal-polymers are highly heat-resistant.

Keywords: electropolymerization, 2-aminothiazole, metal-containing coating, cyclic voltammetry, polymer matrix

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Preparation and properties of electrochemically active polymers, especially metal-containing ones, are of special interest due to their promising applications in medical devices, environmental express test kits, and solar energy converters [1–4]. Recently, electrodes surface has been often modified with organic conductive polymer based on 2-aminothiazole.

It has been demonstrated that 2-aminothiazole is electrochemically active and can readily cover electrode surface with polymer layer, highly resistant in corrosive media [5, 6]. The polymer structure allows application of 2-aminothiazole-based polymers as conductive matrix for incorporation of metal particles via electrodeposition from the corresponding salt solution, thus yielding new nanocomposite materials [3, 7, 8]. The so formed metal clusters are stabilized in the polymer by interaction with nitrogen-containing groups.

In this work, we performed electropolymerization of 2-aminothiazole either in the oscillating potential mode, at 0.2–1.8 V (Ag/AgCl), or in the galvanostatic mode.

Metal-containing nanocomposite polymeric coatings were then formed via deposition of Rh(III) from solution of Na_3RhCl_6 in aqueous nitric acid into the poly(2-aminothiazole) film accompanied with reduction of Rh(III) to Rh(0) at negative external potential. The so formed metal atoms are likely stabilized due to the interaction with donor nitrogen atoms of the polymer matrix [6].

Electrochemical reduction of rhodium was performed during 180, 300, or 420 s, and then the cell circuit was switched off. Using the quartz electrochemical microbalance we demonstrated that the amount of deposited rhodium was a function of time of keeping 2-aminothiazole-modified electrode in the salt solution at –0.4 V as well as of time of subsequent maintaining under the open circuit conditions. Hence, the metal ions could likely be chemically reduced by certain active sites of the polymer matrix.

The formation of the metal-containing coatings was further confirmed by cyclic voltammetry of the initial films and the films after electrodeposition (Fig. 1). In the case of the metal-containing films, electrochemical reduction of protons was observed at negative potential, being typical of metals of platinum group. In the case of initial poly(2-aminothiazole) film no hydrogen release was observed at that potential range.

From data in Fig. 1 it is evident that longer presence of the film in the salt solution at –0.4 V led to higher current of protons reduction (at $E < -0.20$ V); in other words, longer electrodeposition increased the amount of deposited rhodium.

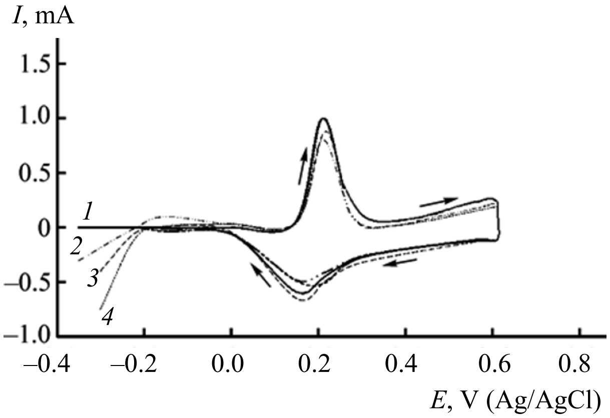


Fig. 1. Cyclic voltamperograms of the initial poly(2-aminothiazole) film (*1*) and the films modified via electrodeposition of metal rhodium during 180 (*2*), 300 (*3*), and 420 s (*4*). Potential change rate of 30 mV/s.

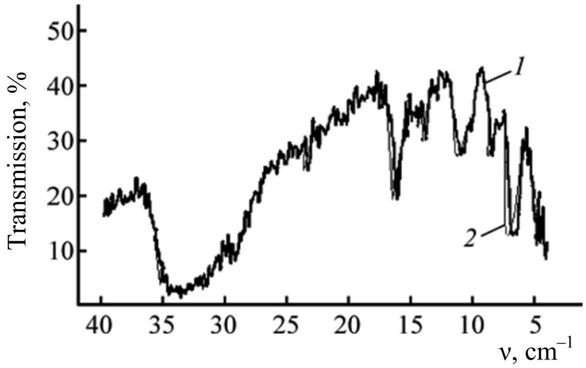


Fig. 2. IR spectra of the initial (*1*) and rhodium-modified (*2*) poly(2-aminothiazole) films.

IR spectra of the metal-containing poly(2-aminothiazole) films (Fig. 2) contained broad bands of stretching (3170–3530 cm^{-1}) and deformation (1630–1670 cm^{-1}) vibrations of conjugated amino and imino groups along with bands of medium intensity at 1260–1420 cm^{-1} assigned to vibrations of thiazole rings. Noteworthily, in the presence of metal rhodium all the characteristic absorption bands shifted to higher frequencies by 10–30 cm^{-1}, pointing at the metal interaction with binding sites of the polymer.

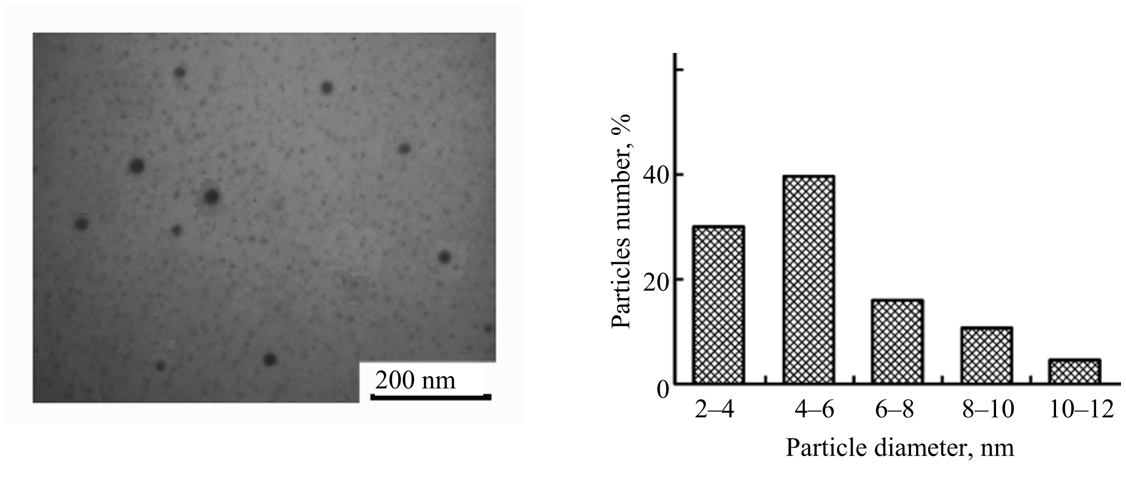
Size distribution of the deposited rhodium particles was determined by transmission electron microscopy (Fig. 3). According to the microscopy results, rhodium particles of 2–12 nm in diameter were uniformly distributed in the polymer matrix.

Thermogravimetric measurements demonstrated high heat-resistance of the prepared metal-containing polymer films: their decomposition onset was at 265°C.

To conclude, we have demonstrated preparation of polymer films based of poly(2-aminothiazole), modified with uniformly distributed relatively monodisperse rhodium nanoparticles.

EXPERIMENTAL

2-Aminothiazole-based polymer films were prepared by electropolymerization of 2-aminothiazole in the three-electrode glass cell under conditions of oscillating potential. Preparative electrochemical synthesis of poly(2-aminothiazole) was carried out under galvanostatic conditions at the glassy carbon


(a)

(b)

Fig. 3. Representative TEM picture of metal-containing film of poly(2-aminothiazole) (a) and size distribution of the rhodium particles (b).

electrode surface (*S* of 1–2 cm^2, *j* of 0.65–0.70 mA/cm^2) during 30–40 min.

IR spectra of the films (KBr) were recorded using the Specord M-80 spectrometer.

Preparation of the films and their electrochemical studies were carried out using the PI-50.1 potentiostat-galvanostat equipped with the PR-8 programming unit.

Transmission electron microscopy studies of the films were carried out using the LIBRA 200 FE microscope (Carl Zeiss, Germany). The specimens were prepared by transfer of the film fragments onto the copper grid. Content of the metal in the composites was determined via atom absorption analysis applying the Perkin Elmer Analyst 200 spectrometer (USA).

Thermogravimetry experiments were carried out using the MOM derivatograph (Hungary) at the heating rate of 5 deg/min.

The metal-containing films were prepared as described elsewhere [9]. The electrode covered with the priorily formed poly(2-aminothiazole) film was immersed in the aqueous solution of HNO_3 (1 mol/L) and Na_3RhCl_6 (5 mmol/L), and the potential of –0.4 V was applied during 180, 300, or 420 s; then the electrode was left in the same solution without any external potential applied.

Monomer 2-aminothiazole was prepared and purified as described elsewhere [10]; colorless crystals with mp 91–92°C.

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