



Electrochemical preparation of composite coatings of 3,4-ethylenedioxythiophene (EDOT) and 4-(pyrrole-1-yl) benzoic acid (PyBA) with heteropolyanions



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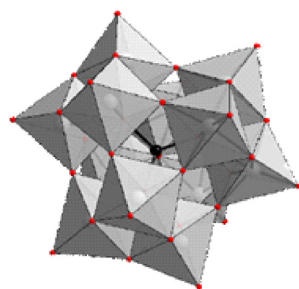
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HIGHLIGHTS

- The composite SiMo₁₂-PEDOT/PyBA coatings on carbon and steel substrates were investigated.
- The coatings have exhibited very good adhesion to the substrate.
- The coatings are capable of largely blocking the access of chlorides anions.

GRAPHICAL ABSTRACT



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ABSTRACT

The possibility of incorporating 4-(pyrrole-1-yl) benzoic acid, (PyBA), and heteropolyacids (SiMo₁₂) during the electrodeposition of poly (3,4-ethylenedioxythiophene), PEDOT, is demonstrated in the paper. The formed novel composite material was applied on the electrode surface as a moderately thin (ca. 0.9–1 μm thick) PEDOT/PyBA/SiMo₁₂ coating. The physicochemical identity of our composite coating was established with the use of electrochemical, spectroscopic, and microscopic techniques. The fact that carboxylate-containing PyBA units link with positively charged and PEDOT structures tend to improve the overall stability and adherence of composite coatings to glassy carbon and stainless steel. The PEDOT/PyBA composite serves as a stable host matrix for large negatively charged silicium heteropolytungstates inorganic species. Consequently, due to the formation of denser polymeric structures and due to the existence of electrostatic repulsion effects, the large polyanion-containing composite coatings are capable of blocking the access of smaller pitting-causing anions (chlorides) to the surface of stainless steel.

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1. Introduction

Over the last several years, there has been growing interest in conducting polymer coatings on electrodes [1–13] due to the

prospects of their application in various microtechnological systems, including charge storage devices, sensors, gas separating membranes, molecular electronics, displays and light emitting diodes, and corrosion protection. From among the many conducting polymers, poly(3,4-ethylenedioxythiophene) or PEDOT has been recently of interest as a particularly stable, highly conductive and electroactive organic polymer [14–20]. For example, PEDOT has

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been used as an antistatic coating [21], a conductive electrode in light emitting diodes [22], and as a material for electrochromic devices [23]. It is commonly accepted that PEDOT is very stable in the doped (oxidized) state [24], and it may reach a conductivity as high as 200 S cm^{-1} [25]. Although the latter parameter is dependent on the coating morphology, methods of preparation, measurement and experimental conditions, and it has been reported to be lower by approximately an order of magnitude under *in situ* conditions [26], the overall conductivity of the polymer is high in the oxidized state [27]. The exact nature of the electrochemical processes occurring in the PEDOT coating is fairly complex, and the system is believed to undergo several overlapping fast redox transitions characterized by high diffusion coefficients for charge propagation. The above properties make PEDOT attractive as a potential material for fabrication of composite matrices with immobilized metals [13,20,28,29].

PEDOT and its derivatives have been recognized as the most stable conducting polymer systems currently available. PEDOT coatings can be formed either chemically or electrochemically, and the overall polymerization involves the oxidation of the 3,4-ethylenedioxythiophene (EDOT) monomer, typically performed in organic non-aqueous solvents rather than in aqueous solutions [30]. The possibility of using aqueous anionic micellar media containing sodium dodecyl sulphate for making PEDOT coatings on electrode surfaces was shown [31]. The possibility of incorporating 4-(pyrrole-1-yl) benzoic acid (PyBA) during the electrodeposition of PEDOT was demonstrated recently [32]. The morphology of the resulting PyBA-modified PEDOT coatings was found to be granular and much denser compared to the PyBA-free PEDOT. Upon the incorporation of PyBA, the overall stability of the PEDOT coatings (resistance to dissolution) was improved.

The purpose of this study was to develop the means of improving the dissolution of the EDOT monomer in an aqueous solution, as well as to stabilize the surface of the glassy carbon and steel substrate during the electrodeposition of PEDOT-based composite coatings and during oxidative voltammetric potential cycling. We have proposed a novel preparative solution consisting of PyBA with PEDOT and containing Keggin-type polyoxometalate, such as silicododecamolybdic acid ($\text{H}_3\text{SiMo}_{12}\text{O}_{40}$). The first carboxylate-derived organic component was demonstrated to form (with Prussian blue) crack-free composite materials to be used in the construction of optical [33] and amperometric sensors [34]. Another important issue is that the positively charged polymer (PEDOT) backbones are not only stabilized with carboxylate-containing PyBA units, but also attract electrostatically robust inorganic polyanions. In addition to the stabilization effect, it is noteworthy that the anion exchange membrane properties of the conducting polymer are reversed, and the composite system (protective coating) starts to repel anions (including pitting chlorides). Finally, the existence of silicium heteropolymolybdates may stabilize the interface formed at the steel surface presumably by forming sparingly soluble ultra-thin deposits [with chromium(III) and iron(II) or iron(III)] on the steel. We have established the physicochemical identity of our composite coating using electrochemical, spectroscopic, and microscopic techniques.

2. Experimental

All chemicals used were of analytical grade purity. The electropolymerization of PEDOT/PyBA was performed in an aqueous medium consisting of $0.068 \text{ mol dm}^{-3}$ 3,4-ethylenedioxythiophene (Aldrich), 10 mg of 4-(pyrrole-1-yl) benzoic/PyBA (Aldrich) in 1 dm^{-3} of water. Heteropolyacids, $\text{H}_3\text{SiMo}_{12}\text{O}_{40}$ (SiMo_{12}), were obtained from Fluka. Solutions were prepared using doubly

distilled and subsequently deionized (Millipore Milli-Q) water. Experiments were carried out at room temperature.

Electrochemical measurements were performed using a CH Instruments (Model CHI 660) workstation (Austin, USA). A glassy carbon disk (with a geometric area of 0.2 cm^2) supplied by Mineral (Warsaw, Poland), or an X20Cr13 stainless steel (C, 0.17%; Cr, 12.6%; Si, 0.34%; Ni, 0.25%; Mn, 0.30%; V, 0.04%; P, 0.024%, and S < 0.005%) disk (with a geometric area of 0.2 cm^2) embedded in epoxy resin acted as a working electrode. The experiments were performed in a conventional three-electrode system, where platinum wire served as a counter electrode, while an Ag/AgCl electrode was the reference electrode.

Prior to each experiment, the (stainless steel) electrode surfaces were polished with waterproof emery paper (Nos. 600, 1000 and 2000) and rinsed with distilled water. The glassy carbon electrode was activated by polishing it with aqueous alumina slurries (with a grain size of $0.05 \mu\text{m}$) on polishing cloth and then rinsed with distilled water.

Unless indicated otherwise, SiMo_{12} -containing PEDOT/PyBA (PEDOT/PyBA/ SiMo_{12}) coatings were produced on glassy carbon and on stainless steel by cycling the potential from -0.2 to 1.0 V for a duration of 1056 s at 50 mV s^{-1} in a modification solution containing 30 mmol dm^{-3} SiMo_{12} and $0.068 \text{ mol dm}^{-3}$ EDOT (together with 10 mg of PyBA in 1 dm^{-3} water). To describe the corrosion behaviour of uncoated and coated samples, potentiodynamic polarization curves were recorded at a scan rate of 10 mV s^{-1} by varying the potential between -0.8 and 1.6 V (vs. Ag/AgCl) in acidified 0.5 mol dm^{-3} K_2SO_4 ($\text{pH} = 2$) solutions with the addition of 0.5 mol dm^{-3} KCl.

The coating thicknesses were determined using a profilometer (Talysurf 50, Rank Taylor Hobson). The thickness of the PEDOT/PyBA/ SiMo_{12} coating, as determined based on the data obtained using the profilometer, was equal to $0.95 \mu\text{m}$. The coating was deposited on glassy carbon. Scanning electron microscopy (SEM) images were produced using a JOEL. The coating was deposited on stainless steel. Inverted microscope images were obtained using OLYMPUS Model GX71. Infrared spectra were measured with a Shimadzu 8400 Fourier transform infrared (FTIR) spectrometer.

In the present work we present the coating adhesion investigations which were performed by scratch tape test. Before the adhesion test the modified electrode was rinsed with distilled water and dried in the ambient conditions. Next the scotch tape was stuck to the surface. The tape was detached rapidly. The amount of modified material on the scratch tape indicated the adhesivity of the surface coating. Only after ten times of detaching of scotch tape from the PEDOT/PyBA/ SiMo_{12} coating there was observed the beginning of decohesion process. This kind of adhesion test allows to assess how strongly the coating is attached to the substrate.

3. Results and discussion

3.1. Fabrication of polyoxometalate/PEDOT/PyBA coatings

The controlled electrodeposition of composite coatings of PEDOT/PyBA with Keggin-type SiMo_{12} heteropolyanions was conveniently achieved by voltammetric potential cycling in respective modification mixtures, as described in [Experimental section](#). [Fig. 1A](#) illustrates the growth of the SiMo_{12} -PEDOT/PyBA coating, as evidenced by the increase in the peak currents, during the first 22 voltammetric cycles. The further growth of the coating during potential cycling was much slower. Due to the possibility of SiMo_{12} structural reorganization, the negative potential excursions were limited to -0.2 V in [Fig. 1A](#).

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