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Synthesis and characterization of chemically and electrochemically prepared conducting polymer/iron oxalate composites

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Abstract

Poly(3-octyl-thiophene) (POT) and polypyrrole (PPy) iron oxalate composites were synthesized through a post-polymerization oxidative treatment. The composite of the latter has been prepared also by electrochemical polymerization. The samples have been characterized by X-ray diffraction (XRD), impedance spectroscopy, scanning electron microscope (SEM) combined with energy dispersive X-ray (EDX) spectroscopy, Mössbauer spectroscopy, cyclic voltammetry and electrochemical quartz crystal microbalance (EQCM). In case of PPy, two peaks in the XRD spectra show the presence of iron containing composite, while with POT only the layered structure originating from the octyl side-chain interactions was modified by the composite formation. The assumption of the weakening of short- and long-range interactions was proven by the decrease in conductivity of the composite. The successful electrochemical synthesis resulted a composite of ~5% iron content, determined by EDX. Mössbauer spectroscopy measurements evidenced a composite containing mixed valence iron oxalate doping ions, which supports the indirect EQCM data.

Keywords: Conducting polymers; Composites; Iron oxalate; EQCM; Mössbauer spectroscopy

1. Introduction

Electronically conducting polymers [1–4] have a considerable electric resistance that is generally associated with semi-conductor behaviour, while upon oxidation or reduction they can be transformed into a metallic – conducting – state, as well [5]. The electrochemical transformation between the neutral and oxidized states has been widely studied in numerous laboratories [6–11]. Composites of these polymers with inorganic matter, combining together the different properties of components, provide new opportunities therefore they are considered remarkable advanced materials.

During the past decade, a new branch of materials science – nanostructured materials – has developed, and the special character of nanosized solid materials has received intense attention. Recently, the importance of metal nanoparticles has been summarized in a feature article [12], emphasizing the photophysical, photochemical, and photocatalytic aspects resulting unique electronic and chemical properties. The importance of such composites lies in the special opportunities these materials open in the development of a new generation of nanodevices.

Nanocomposite materials based on conjugated polymers may contain the conducting component either dispersed in inorganic matrix [13] or, vice versa, the conductive organic matrix may incorporate the other phase. Conjugated polymers have been successfully applied as the conducting matrixes of composite materials incorporating noble metals, *e.g.* Pd, Au, or Pt [14–17], and previous work in our group demonstrated a simple procedure for preparing polypyrrole/Ag nanocomposites [18]. Other works on polymer nanocomposites reports on the incorporation of TiO_2 [19–20], Nb_2O_5 [21], V_2O_5 [22] or iron oxide [23–25]. Recently an interesting PANI/iron oxalate composite [26] was synthesized through a post-polymerization oxidative treatment. As it is well known, iron oxalate is photo-sensitive, and it decomposes at a 100% quantum yield. On the basis of this property it is applied in energy meter devices. From Mössbauer spectroscopic results obtained with this special composite, the authors assumed the incorporation of a mixed valence iron oxalate into PANI.

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In this work our aim was to study the formation of iron oxalate composite in combination with POT and PPy. Medium chain length alkyl-thiophenes show supramolecular structure [27] due to interchain interactions, and the interstitial space between polymer segments may insure the incorporation of the organic matter. The formation of a mixed valence $[Fe(II)Fe(III)(ox)_3]^-$ is important as a redox active component, with paramagnetic behaviour.

2. Experimental

Chemicals were purchased from Sigma–Aldrich. All reagents were analytical grade. Water was purified by deionization and reverse osmosis (Milli-Q).

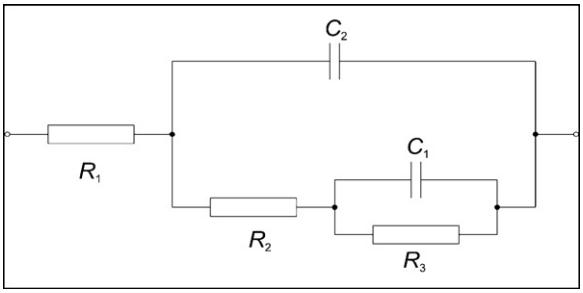
POT powder was chemically synthesized through the oxidation of the monomer by $FeCl_3$ in water-free chloroform solutions. The product obtained was filtered and washed thoroughly with ethanol to remove ferric or ferrous contamination. The POT/iron oxalate composite was prepared by the following method. In the first step, 1.5 mmol $FeCl_3 \cdot 6H_2O$ and 3.75 mmol $(NH_4)_2C_2O_4 \cdot H_2O$ were dissolved in 10 ml distilled water to obtain a clear green solution of iron oxalate. Next, 0.25 g of POT was added to this solution with constant stirring. Then 6.35 mmol of 30% H_2O_2 was added. The powder obtained was filtered, washed with distilled water and dried in air [26]. The dried powder was used in the XRD experiments. Some portions of the substance were compressed into pellets for the conductivity measurements, by applying a pressure of $p = 740$ MPa. The diameter and the thickness of the pellets was 13 mm and 2 mm, respectively.

Pyrrole was freshly distilled under vacuum. PPy powder was chemically synthesized through the oxidation of the monomer by $Fe(NO_3)_3$ in aqueous solutions. The powder obtained was filtered, washed thoroughly with water to remove any residues from the oxidant. The PPy/iron oxalate composite was prepared by the foregoing method.

The composites were measured by wide-angle X-ray diffraction (WAXRD) (Philips PW-1830 X-ray diffractometer). For irradiation the Cu Kα line, $\lambda = 0.1542$ nm was applied (cathode at 40 kV and 30 mA), and Bragg scattering was recorded in the range of $2\Theta = 2$–80°.

The impedance spectra [28] were obtained by using an SR830 lock-in amplifier. It was operated in remote mode via the RS232 interface and programmed by the computer host in LabVIEW 7.1 version. Impedance spectroscopy data were measured in the dry state in the frequency range 10 Hz–10 kHz, and were fitted using the model circuit comprising ohmic and capacitive elements, frequently applied for the characterization of the non-conducting state of conjugated polymers [29] (Scheme 1). Although we did not measure under polarization, data were fitted to this model circuit, and the largest resistance was used to calculate the conductivity of the pellets.

The PPy/iron oxalate films were first deposited potentiostatically, at 0.65 V potential and for 60 mC/cm^2 charge density from a solution of 0.1 M for the pyrrole and saturated iron(II) oxalate. PPy/DS films were also synthesized under the same conditions except that the deposition solution contained 0.1 M sodium dodecyl sulphate (SDS) instead of the iron(II) salt. We prepared PPy layer also in the presence of a mixture of the two salts (PPy/DS/iron oxalate). The working electrode was platinum ($A = 0.5$ cm^2). Ag/AgCl/3.4 M KCl microelectrode (LF-2, Innovative Instruments Inc.) and a platinum foil were used as reference and counter electrodes, respectively. After the electro-polymerisation the films were left to relax [30]. Cyclic voltammograms of the three films were registered in 0.1 M SDS monomer-free solutions at 10, 25, 50 and 100 mV/s sweep rates. The electrochemical measurements were done on a PGSTAT 10 (Autolab) instrument. Large-scale synthesis of the composite was performed galvanostatically at $I = 3$ mA/cm^2 current density. PPy/iron oxalate films were peeled off from the Pt electrode and air-dried for SEM, EDX and Mössbauer spectroscopy investigation.



Scheme 1. Equivalent circuit for modelling the polymer film. R1: electrolyte resistance, C1: double layer capacitance, R2 resistance of the layer, C2 charge transfer capacitance, R3 charge transfer resistance.

In the case of the EQCM measurement polypyrrole film were deposited galvanostatically also at a 3 mA/cm^2 current density and for 60 mC/cm^2 charge density from a solution of 0.1 M for the monomer and saturated iron(II) oxalate. This charge density (and layer thickness) was chosen in order to exclude viscoelasticity [31]. The working electrode was an Au coated quartz crystal ($A = 0.196$ cm^2). The reference electrode was Ag/AgCl. The EQCM measurements were carried out by using a quartz-crystal analyzer (QCA917, EG&G Seiko).

Hitachi S-4700 scanning electron microscopy (SEM) was used to investigate the morphology of the samples, coupled with Energy Dispersitive X-ray Microanalysis (EDX, Röntec QX2), to get further information on the composition.

^{57}Fe Mössbauer spectrum of the sample was acquired with a 10^9 Bq ^{57}Co(Rh) source in transmission geometry. The isomer shift values are given relative to α-iron.

3. Results and discussion

3.1. POT-based composite

Chemically synthesized POT powder was stirred with in situ formed iron(III) oxalate complex solution in the presence of hydrogen peroxide, and the resulted – powder-like – material was studied by XRD. The spectrum is presented in Fig. 1 in comparison with that of POT alone (curve a). POT can be characterized by two distinct signal groups: the "hill" at 15–28° is connected to amorphous phase, while the reflections at around