

Electrochemical (redox) behaviour of microporous polyethylene-based conducting polypyrrole composites

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Abstract. The redox behaviour of an electrically conductive composite obtained by gas-phase oxidative polymerization of pyrrole on the microporous polyethylene (PE) film [PE-PPy(Cl)] was investigated by cyclic voltammetry. It was found that the composite is electrochemically active in aqueous NaCl solution. The possibility of modification of this composite by electrochemical deposition of an additional polypyrrole layer was demonstrated. The redox behaviour of the obtained new polymeric electrically conductive composite structure (PE-PPy(Cl)/PPy(X)_{el}), where X⁻ is doping anion (Cl⁻, NO₃⁻, *p*-toluensulphonate, naphthalene sulphonate, dodecyl benzene sulphonate), was investigated. Doping anions and the thickness of the electrochemically deposited PPy layer were found to influence the cation and/or anion exchange during the redox processes in the new composite structure. The stability of the redox processes in the composite structure was tested in aqueous NaCl solution with continuous cycling up to 100 times. It was shown that the composite structure that contains small inorganic anions such as Cl⁻ or NO₃⁻ is electrochemically more stable than that with large organic anions (naphthalene sulphonate).

Key words: polypyrrole, polyethylene, composite, cyclic voltammetry.

INTRODUCTION

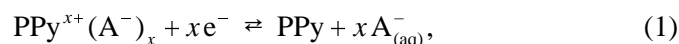
Conducting polymers have taken a prominent place in the research world because of their electrical, electrochemical, and optical properties and their

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possible applications in organic batteries [1], sensors [2], microelectronic devices [3], gas separation technology [4], ion-exchange membranes [5], anti-corrosion coatings [6], and artificial muscles [7]. Polypyrrole (PPy) is one of the representative conducting polymers due to its high stability and rather easy synthesis. PPy can be prepared either by the electrochemical polymerization method or by the chemical oxidative polymerization method. Most PPys thus prepared are insoluble, infusible, and have poor mechanical properties, which restricts the area of their application. One of the ways of obtaining these polymers with desired mechanical properties is the combination of conducting polymers with conventional polymers by creating composites or blends. PPy composites with different polymers – polycarbonate [8], polypropylene [9], and polyamide [10] – have been studied. One of the most promising substrates for PPy composites seems to be microporous polyethylene (PE), as it has good mechanical properties and high chemical resistivity to aggressive media. A new type of microporous PE (0.01–0.5 μm pores) was obtained by a technique based on the PE melt extrusion [11]. An electrically conducting composite of PPy and microporous PE was prepared by polymerization in the gas phase [12]. The properties of this PE–PPy(Cl) composite have been studied by different methods: ultrafiltration, gas separation, electro dialysis [12], thermogravimetry, differential thermal analysis, and wide-angle X-ray scattering [13]. As it was established [12], the PE–PPy composite systems have good mechanical characteristics. Moreover, the major advantage of this composite is a high adhesion of PPy to the microporous PE film, provided by the specific properties of its surface (developed relief-like character and porous structure). Owing to the conducting polymer layer the initially hydrophobic microporous PE film becomes a hydrophilic ion-exchange membrane with high selectivity to anions [12]. The electrochemical properties of PE–PPy(Cl) have been studied by measuring the electrolytic resistance and concentration potentials of the membranes [14]. However, the redox behaviour of these membranes in aqueous solutions has, to our knowledge, not been described in the literature.

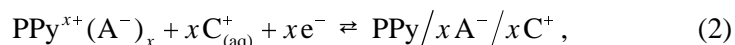
The electrochemical behaviour of conducting polymers has been extensively studied with the aim of elucidating the nature of ionic doping, conduction, and charge accumulation in these materials. Diverse electrochemical and non-electrochemical techniques have been used for this purpose, among them cyclic voltammetry [15], electrochemical impedance spectroscopy [16], and quartz crystal microbalance [17].

It was demonstrated [18–21] that the redox properties of the conducting polymer depend strongly on the nature of the anion incorporated during synthesis. In PPy films prepared with small doping anions such as Cl^- or NO_3^- the charge is compensated by insertion of the anions during oxidation (doping) and release of the same anions during reduction [18]:



where A^- is doping anion and x is doping level.

When PPy is prepared with large organic anions such as naphthalene-sulphonate (NS^-), the charge compensation involves incorporation of cations, since the mobility of the anions in the matrix is low [19].



where C^+ is cation of electrolyte.

When PPy is doped with medium-sized anions such as *p*-toluenesulphonate (TOS^-), both anions and cations participate in the redox process of PPy [20]. On the other hand, these doping–dedoping processes depend also on the nature of the supporting electrolyte: the relative mobility of these species will determine the anion and cation transport characteristics [21]. Therefore, it appears that the simple anion doping–dedoping, described by Eq. 1, rarely occurs in isolation, and that the total redox process also involves cation incorporation and expulsion according to Eq. 2. The degree to which each of these processes occurs depends on the nature of the polymer material as well as the mobility of the anion and cation in the solution and through the polymer [21].

Taking into account the possible application of PE–PPy(Cl) as an ion-exchange membrane, the investigation of the redox behaviour can provide information about the electrochemical ion-exchange properties of this composite. Further modifications of PE–PPy(Cl) may be useful in gas-separation applications.

In this work the redox behaviour of the PE–PPy(Cl) composite was investigated by cyclic voltammetry (CVA). Also the possibility of performing electrochemical deposition of PPy onto this composite was studied. Electrolytes with different anions X^- (Cl^- , NO_3^- , TOS^- , NS^- , dodecyl benzene sulphonate (DBS^-)) were used for the electrochemical polymerization of pyrrole and for the investigation of the cation and/or anion exchange. The stability of the redox processes in PE–PPy(Cl)/PPy(X)_{el} was tested in an aqueous electrolyte with continuous cycling up to 100 times.

EXPERIMENTAL

Microporous membranes were prepared from a linear high-density PE ($M_w = 140\,000$) in a process based on the melt extrusion technique with subsequent annealing, uniaxial extension, and thermofixation. The thickness of the films was 12–13 μm .

A composite PE–PPy(Cl) membrane was prepared by oxidative polymerization of pyrrole from the gas phase *in situ* on the surface of PE microporous films [12]. The PE porous film was treated with 1 M solution of ferrous chloride in methanol and then suspended in a reaction vessel containing pyrrole vapours at room temperature. The film was washed with methanol and dried. The membranes selected for the present study contained 25.7 wt.% of PPy.

Electrochemical deposition of PPy films on the PE–PPy(Cl) membrane was carried out in a three-electrode cell. For electrode preparation the PE–PPy(Cl)

membrane was attached to a platinum plate with carbon paste. The area of the working electrode was 0.64 cm². A Pt wire was used as a counter electrode and a saturated calomel electrode (SCE) as a reference electrode. PPy electrochemical synthesis was performed galvanostatically at a current density of 2 mA/cm² for 20 min from an aqueous solution containing 0.1 mol/L pyrrole and 0.1 mol/L electrolyte salt (NaCl, NaNO₃, NaTOS, NaNS) at room temperature.

Cyclic voltammetry was performed in 0.1 M NaCl aqueous solution. The potential was cycled from -1100 to +400 mV at a scan rate 5 mV/s. Prior to each experiment, the electrolyte was deaerated by passing nitrogen through the solution for 15 min. A radiometer potentiostat VoltaLabTM32 with software VoltMaster 2 under a direct computer control was used for both synthesis and CVA measurements. The surface conductivity of the prepared composite structures was measured by the standard four-probe method.

RESULTS AND DISCUSSION

Cyclic voltammograms of the composites. Electrodeposition of an additional PPy layer

The voltammogram of PE-PPy(Cl) composite in 0.1 M NaCl aqueous solution is presented in Fig. 1 (curve a). A moderately sharp cathodic peak (E_{pc}) was observed at -610 mV and a broad anodic peak (E_{pa}) around -170 mV. This behaviour clearly illustrates that PE-PPy(Cl) is electroactive in the solution. The electroactivity of this composite membrane is due to the continuous conducting polymer network with redox active centres formed during chemical polymerization of pyrrole inside the PE membrane. As it was established earlier, only 25% of the Cl⁻ ions in PE-PPy(Cl) are in ionic state and are thus able to participate in ion-exchange processes [22]. It is also known that in the PPy films electrochemically synthesized with Cl⁻ doping anions the redox processes occur with participation of both cations and anions [21]. Thus, we suggest that the pair of anodic and cathodic peaks is probably associated with both Cl⁻ and Na⁺ ions insertion/expulsion during the doping/dedoping process taking place in the composite film.

As the electrochemical oxidation and reduction of the polymer involves both electron and ion exchange processes, it is not possible to obtain information on electron transfer and ion exchange processes separately. The fact that anions and/or cations are exchanged between the electrolyte solution and the composite during electrochemical oxidation-reduction suggests that PPy exhibits apparent ion conductivity.

The voltammograms in Fig. 1 were recorded at a relatively slow scan rate (5 mV/s). At the faster scan rates no redox peaks were observed. This indicates that charge transfer processes in the PE-PPy(Cl) composite are retarded due to the thickness of the film. The large peak separation (440 mV) is also related with the slow charge transfer process and film thickness [23].

We could successfully perform electrodeposition of the additional PPy layer onto the electrically conductive PE-PPy(Cl) substrate. The voltammogram of the resulting PE-PPy(Cl)/PPy(Cl)_{el} composite structure in 0.1 M NaCl solution is presented in Fig. 1 (curve b). As a result, the current of anodic and cathodic peaks increased and the area of the voltammogram became larger as compared to PE-PPy(Cl). The increased electroactivity of the composite structure can be explained with the increase in the thickness of the PPy layer and/or with the better redox properties of the electrodeposited PPy film. Also, the second reduction wave at more negative potential, which is probably associated with cations (Na⁺) insertion during polymer reduction, appears in this case. The corresponding oxidation wave for this process (i.e. the cation expulsion during oxidation) is not obvious in the reverse sweep. A similar behaviour (with one oxidation and two reduction peaks) was observed in the voltammograms of the electrodeposited PPy(Cl) on the Pt electrode (Fig. 1, curve c). It was established by the electrochemical quartz crystal microbalance (EQCM) method that both anions and cations are involved in the redox process in the Au/PPy(Cl) system [24]. Therefore, it seems that the anodic peak is associated with both the anions insertion and cations expulsion processes. Compared to the Pt/PPy system the anodic peak potential of the PE-PPy/PPy(Cl)_{el} system is more positive, which probably indicates a slower charge transfer process during the polymer oxidation in this case.

On the voltammograms presented in the Fig. 1 it can be seen that in all cases the broad anodic peak due to the polymer oxidation is followed by a capacitive current plateau at the positive potentials. As it was demonstrated by Paasch et al. [25] and others [26] this “capacitive” behaviour is related to the continuous faradic charge transfer at the potential beyond the first oxidation wave in the cyclic voltammogram. Also it can be seen that the initial potential values of the anodic wave (E_{0p}) are almost identical for all three samples presented in Fig. 1.

Electrochemical characteristics of PPy films and composites in 0.1 M NaCl aqueous solution obtained from the cyclic voltammograms (Fig. 1) are summarized in Table 1.

Table 1. Electrochemical characteristics of polypyrrole films and composites in 0.1 M NaCl aqueous solution obtained from voltammograms (Fig. 1)

Characteristic	PE-PPy(Cl)	PE-PPy(Cl)/PPy(Cl) _{el}	Pt/PPy(Cl)
Initial potential of anodic wave (E_{0p} , mV)	-575	-585	-630
Anodic peak potential (E_{pa} , mV)	-170	212	-26
Anodic peak current density (i_{pa} , mA/cm ²)	0.3	2.7	1.7
Cathodic peak potential (E_{pc} , mV)	-610	-199	-204
		-879	-850
Cathodic peak current density (i_{pc} , mA/cm ²)	0.5	1.2	1.1
		1.2	0.7
Peak separation ($\Delta E = (E_{pa} - E_{pc})$, mV)	440	411	178

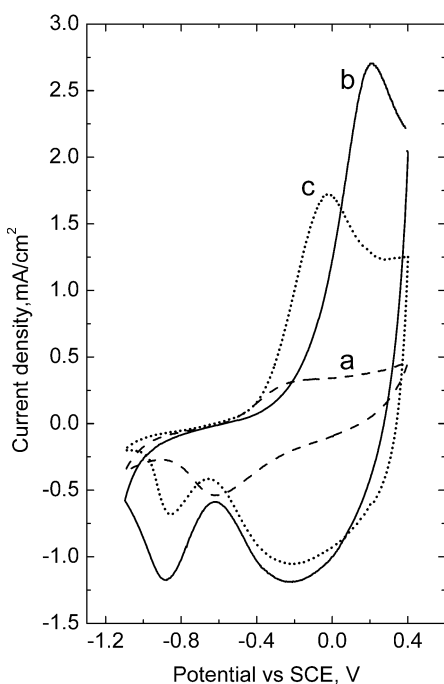


Fig. 1. Cyclic voltammograms of PPY composite electrodes in 0.1 M NaCl aqueous solution, scan rate 5 mV/s: (a) PE-PPy(Cl); (b) PE-PPy(Cl)/PPy(Cl)_{el}; (c) Pt/PPy(Cl).

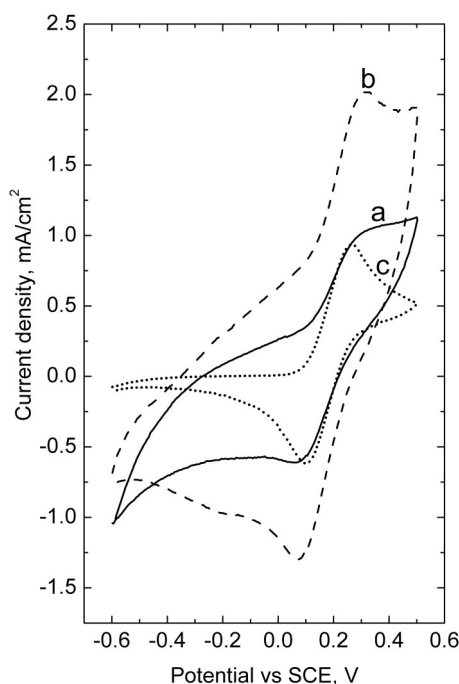


Fig. 2. Cyclic voltammograms of PPY composite electrodes in 0.1 M NaCl aqueous solution containing 0.1 M K₄[Fe(CN)₆], scan rate 5 mV/s: (a) PE-PPy(Cl); (b) PE-PPy(Cl)/PPy(Cl)_{el}; (c) bare Pt electrode.

The electrochemical activity of the composites PE-PPy(Cl) and PE-PPy(Cl)/PPy(Cl)_{el} was also confirmed by cycling in the electrolyte solution containing redox active species of K₄[Fe(CN)₆]. On the voltammograms (Fig. 2, curves a and b) the pair of peaks due to oxidation and reduction of the ferrocyanide ion Fe(CN)₆³⁻/Fe(CN)₆⁴⁻ is present. On the voltammogram of the PE-PPy(Cl) composite these peaks are not well defined compared with the voltammogram of bare platinum (Fig. 2, curve c). Obviously, this is due to the thickness and porous structure of PE-PPy(Cl). In the case of PE-PPy(Cl)/PPy(Cl)_{el} the peaks associated with the Fe(CN)₆³⁻/Fe(CN)₆⁴⁻ couple are sufficiently well defined, but the large peak separation indicates that the redox process is not as reversible as on bare platinum.

Influence of the thickness of the electrodeposited PPY film on the redox behaviour of the composite system

Taking into account that the PE-PPy(Cl) composite film has a porous structure, it is difficult to determine precisely the thickness of the electrodeposited PPY layer. The thickness of the PPY layer was estimated from the

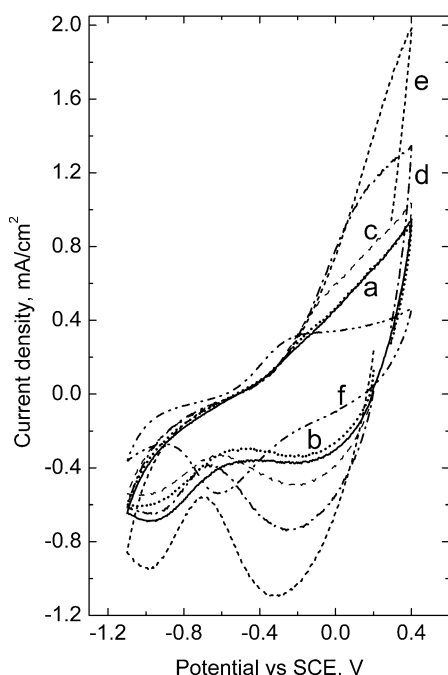


Fig. 3. Cyclic voltammograms of PE-PPy(Cl)/PPy(Cl)_{el} composite in 0.1 M NaCl aqueous solution, scan rate 5 mV/s; different times of electrodeposition of PPy: (a) 100 s; (b) 200 s; (c) 400 s; (d) 800 s; (e) 1600 s; (f) substrate without electro-deposited PPy [PE-PPy(Cl)].

the polymer film. As a result the ratio of the heights of the first and the second cathodic peak becomes different for the composite with thinner and thicker electrodeposited PPy layers.

Influence of doping anions of the electrodeposited PPy film on the redox behaviour of the composite system

Electrolytes with different anions X^- (Cl^- , NO_3^- , TOS^- , DBS^-) were used for the electrodeposition of PPy onto the PE-PPy(Cl) composite. The new composite structure (PE-PPy(Cl)/PPy(X)_{el}) was investigated in 0.1 M NaCl aqueous solution. As it can be seen in Fig. 4 (curves a and b), on the voltammograms of the composite system containing small inorganic anions (Cl^- and NO_3^-) one oxidation and two reduction peaks are clearly distinguished. The identity of these voltammograms is obviously due to the similar values of ion sizes and the mobility of Cl^- and NO_3^- anions. It is necessary to note that in this case the shape of the voltammograms is similar to that of PPyCl or PPyNO₃ on the Pt electrode

charge used for electropolymerization, which is proportional to the synthesis time. Varying the deposition time, PPy layers of different thickness were obtained, assuming that 0.4 C/cm² corresponds to 1 μm of PPy layer [27].

As it can be seen in Fig. 3 (curves a and f), the shape of the voltammogram changed after 100 s of PPy electrodeposition onto PE-PPy(Cl). The anodic and the first cathodic peak shift to the positive potential direction and the second cathodic peak appears at about -900 mV. With increasing electrodeposition time (of film thickness) the peak currents as well as the electroactivity of the composite gradually augment. It is interesting to note that the evolution of the first and the second cathodic peak with increasing PPy film thickness is different. The first cathodic peak, associated with anions expulsion from the PPy film, enhances in series as the polymer film thickness increases (except a and b). No such behaviour can be observed in the evolution of the second cathodic peak, associated with cations insertion in the

obtained in the NaCl solution. In spite of the similarity, the surface conductivity of PE-PPy(Cl)/PPy(Cl)_{el} is 6.2 times greater than that of the PE-PPy(Cl)/PPy(NO₃)_{el} composite (Table 2).

The voltammogram of the composite structure containing TOS⁻ ions has a shape completely different from that of PPyTOS on the Pt electrode, which usually has two pairs of peaks corresponding to the anions and cations exchange between the polymer film and the electrolyte. In our case (Fig. 4, curve c) no peaks corresponding to the reversible redox reaction can be observed on the surface of the PE-PPy(Cl)/PPy(TOS)_{el} composite film. Only a rise of the cathodic current starting at about -0.6 V and an increase in the anodic current are observed. At the same time for this composite system a high value of surface conductivity was obtained, which was four orders of magnitude higher than that of PE/PPy(Cl) (Table 2).

As regards the electrodeposition of PPy/DBS layer on the PE-PPy(Cl) composite membrane from the NaDBS aqueous solution, no film formation was observed. Probably, the surface-active DBS⁻ anions are oriented towards the polymer surface forming the thin insulating layer, which hinders the PPy film electrodeposition process. The support resistance in the place of contact of the composite with NaDBS aqueous solution measured after the electrolysis process was so great that it was impossible to measure it with the four-probe method.

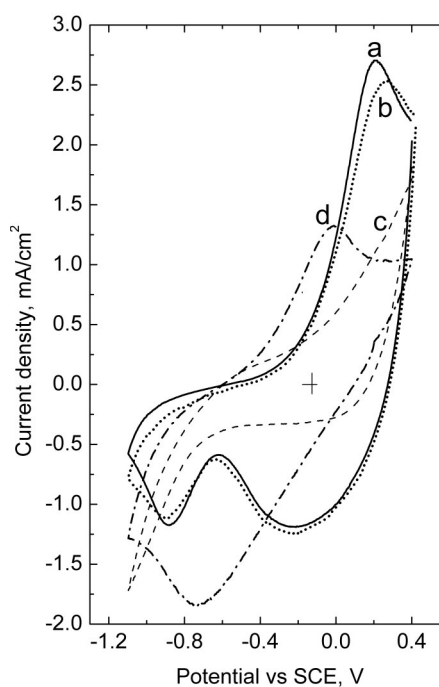


Fig. 4. Cyclic voltammograms of PE-PPy(Cl)/PPy(X)_{el} electrode in 0.1 M NaCl aqueous solution, scan rate 5 mV/s, X⁻ is doping anion: (a) Cl⁻, (b) NO₃⁻, (c) TOS⁻, (d) NS⁻.

Table 2. Surface conductivity of polyethylene-polypyrrole composite films

Sample	Surface conductivity, S/cm
PE-PPy(Cl)/PPy(TOS) _{el}	4.2
PE-PPy(Cl)/PPy(NS) _{el}	1.7
PE-PPy(Cl)/PPy(NS) _{el} after 15 cycles	3.8×10^{-1}
PE-PPy(Cl)/PPy(Cl) _{el}	5.2×10^{-2}
PE-PPy(Cl)/PPy(Cl) _{el} after 100 cycles	3.1×10^{-4}
PE-PPy(Cl)/PPy(NO ₃) _{el}	8.4×10^{-3}
PE/PPy(Cl)	4.1×10^{-4}

According to ref. [28], cation exchange is predominant for the PPy film doped with the large hydrophobic NS^- anion. Therefore, a pair of peaks observed on the voltammogram of the PE-PPy(Cl)/PPy(NS)_{el} composite structure (Fig. 4, curve d) is associated with cation insertion (cathodic wave) and cation expulsion (anodic wave). The cathodic peak on this voltammogram is shifted to more positive potentials compared with the PE-PPy(Cl)/PPy(Cl) composite structure, where first the anion expulsion occurs at about -0.2 V and only after that the cation insertion starts at -0.7 V.

Electrochemical stability

The stability of the redox processes in PE-PPy(Cl)/PPy(Cl)_{el} and PE-PPy(Cl)/PPy(NS)_{el} was tested in aqueous 0.1 M NaCl solution with continuous cycling in the potential range from -1.1 V to 0.4 V (Figs. 5 and 6). The PE-PPy(Cl)/PPy(Cl)_{el} composite structure retains its electroactivity up to 35 cycles. Then, a gradual loss of the electroactivity of the composite is observed and after 100 cycles the electroactivity of the composite film is significantly decreased (Fig. 5). At the same time the surface conductivity of the composite film decreases by two orders of magnitude (Table 2). The PE-PPy(Cl)/PPy(NS)_{el}

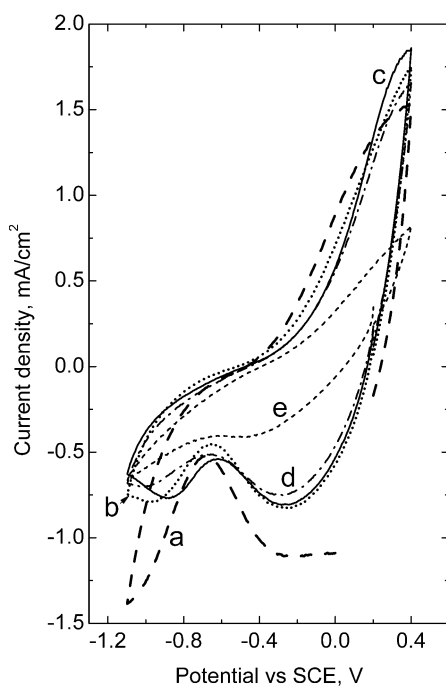


Fig. 5. Continuous cycling of PE-PPy(Cl)/PPy(Cl)_{el} electrode in 0.1 M NaCl aqueous solution, 100 cycles, scan rate 5 mV/s: (a) 1st cycle; (b) 5th cycle; (c) 35th cycle; (d) 50th cycle; (e) 100th cycle.

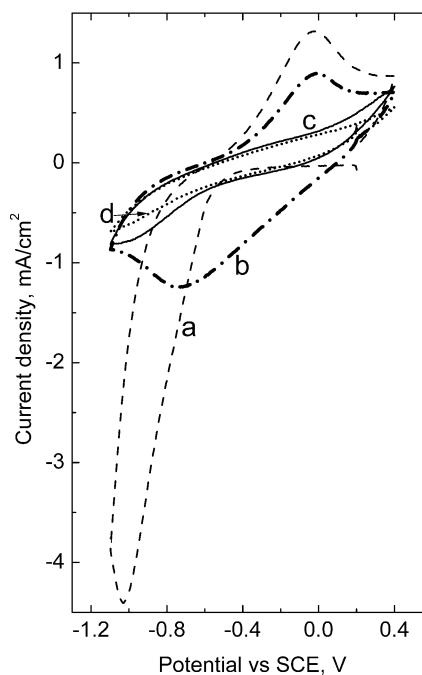


Fig. 6. Continuous cycling of PE-PPy/PPyNS electrode in 0.1 M NaCl aqueous solution, 15 cycles, scan rate 5 mV/s: (a) 1st cycle; (b) 2nd cycle; (c) 5th cycle; (d) 15th cycle.

composite system loses electroactivity in the NaCl solution already after a few cycles (Fig. 6) and the electrical conductivity of the composite film decreases 4.5 times (Table 2).

CONCLUSIONS

The cyclic voltammetry investigation of the electrochemical redox behaviour of the microporous polyethylene-based conducting polypyrrole composite (PE-PPy(Cl)) demonstrated that this composite is electroactive in the aqueous NaCl solution. The modification of the PE-PPy(Cl) composite by electrochemical deposition of an additional layer of polypyrrole was performed for the first time. It was found that such modification allows significant enhancement of the surface conductivity and redox activity. Moreover, it was demonstrated that the thickness of the electrodeposited additional layer of PPy influences the cation and/or anion exchange during the redox processes in the new composite structure. The investigation of the redox behaviour and electrochemical stability of this composite structure with different doping anions (X^-) showed that the composite that contains small inorganic anions (Cl^- or NO_3^-) has better electroactivity and stability in the NaCl aqueous solution than the composite with large anions. In the former composite structures both the cations and anions are involved in redox processes. With a large organic doping anion, such as naphthalene-sulphonate (NS^-), the redox processes occur with the participation of cations.

ACKNOWLEDGEMENTS

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Polüpürrooliga modifitseeritud elektrit juhtiva mikropoorse polüetüleeni elektrokeemilised omadused

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On uuritud gaasifaasist sadestatud elektrit juhtiva polüpürrooli (PPy) ja mikropoorse polüetüleeni (PE) baasil valmistatud komposiidi [PE-PPy(Cl)] redoksomadusi tsüklilise voltamperomeetria meetodil NaCl vesilahuses. Leiti, et valmistatud komposiitkile on NaCl vesilahuses elektriliselt aktiivne. Saadud komposiitkilet modifitseeriti PPy elektrokeemilise sadestamise teel vesilahuses, varieerides sünteesi aega ja elektrolüüti. Erinevate anioonidega legeritud struktuuride PE-PPy(Cl)/PPy(X)_{el} (X = Cl⁻, NO₃⁻, TOS⁻, NS⁻, DBS⁻) redoksomadusi ja stabiilsust uurides leiti, et redoksprotsessid sõltuvad legeriva aniooni valikust ja PPy kile paksusest. TOS⁻ ja NS⁻ ioonidega legeritud kilede elektrijuhtivus oli teistega võrreldes kõrgem. Samas aga Cl⁻ ja NO₃⁻ anioonidega legeritud struktuurid osutusid vesilahustes stabiilsemateks võrreldes suuremate anioonidega legeritud struktuuridega (NS⁻).