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PEDOT films: multifunctional membranes for electrochemical ion sensing

Abstract Properties of electropolymerized poly(3,4-ethylenedioxythiophene) (PEDOT) films were studied from the point of view of direct use as ion-sensing membranes in potentiometric or amperometric sensors. Stable and reproducible potentiometric characteristics were obtained for PEDOT doped by poly(4-styrene-sulfonate) ions, PEDOT(PSS) (cationic characteristics), and PEDOT doped by hexacyanoferrate(II) anions, PEDOT(HCF) (anionic characteristics). As shown by voltammetric and EDAX results, the anion exchange properties of the latter polymer result from gradual replacement of HCF ions by Cl^- anions from solution. The zero-current potentiometric detection limit of PEDOT(PSS), equal to 3×10^{-6} M, can be shifted to 7×10^{-7} M by polarization using a cathodic current density of 3×10^{-7} A cm^{-2}. PEDOT films doped by Cl^- or PSS$^-$ ions can be used as membranes for sensing anions or cations, respectively, under pulse ampero-metric conditions, within the range from 10^{-4} to 1 M, comparable with that accessible by zero-current poten-tiometry. Dissolved oxygen (redox interferent of low charge transfer rate) exerts a minor influence on the slope of the potentiometric and amperometric charac-teristics of PEDOT films. Although the presence of re-dox reactants characterized by a high rate of charge transfer [$Fe(CN)_6^{3-/4-}$] results in the disappearance of the potential dependence on KCl concentration, this disadvantageous effect is much less significant under pulse amperometric conditions.

Dedicated to the memory of Harry B. Mark, Jr. (February 28, 1934–March 3rd, 2003)

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Introduction

Conducting polymers are versatile materials for many applications. They are also very attractive as compo-nents of electrochemical sensors, especially as ion-to-electron transducers for ion-selective electrodes (ISEs), e.g. [1, 2, 3, 4, 5]. However, conducting polymers can be also successfully applied directly as sensing membranes for electrolyte ions, using either a potentiometric [6, 7, 8, 9, 10] or an amperometric mode [11, 12, 13, 14, 15, 16] of measurement. In the case of potentiometry, the mem-brane potential is linearly dependent on the logarithm of the ion activity in the solution. For the amperometric mode of sensing, the ion exchange properties of the partially oxidized (anion exchanger) or reduced (cation exchanger) polymer film coated on the electrode are also of advantage. The oxidation (reduction) current of an anion (cation) exchanging polymer following a potential step application is dependent on the anion (cation) concentration in the solution [11, 12, 13, 14, 15, 16]. The direct use of conducting polymers as ion-sensitive membranes can be attractive, in comparison to more sophisticated systems, owing to the low cost and sim-plicity of sensor preparation. This is an essential advantage from the point of view of, for example, mass production of disposable miniaturized electrodes, where the use of expensive and sensitive chemicals should be avoided, as well as where some steps of chemical mod-ification or physical structuring procedures can be eliminated.

One of the most often used conducting polymers is polypyrrole, which is relatively stable and easy to obtain. However, membranes of this polymer applied directly in potentiometric ion sensors suffer from both low selec-tivity [17, 18] and high susceptibility towards redox

[19, 20] or pH interference [21]. Our latest results showed that when using an amperometric mode of sensing, the role of such interferences could be significantly reduced [22].

Another option is to use a conducting polymer layer as an ion-to-electron transducer, a so-called solid contact for all-solid-state ion-selective electrodes, where high stability of the polymeric material is required. From this point of view, poly(3,4-ethylenedioxythiophene) (PEDOT), as one of the most stable conducting polymers, is especially attractive. Electrochemically obtained PEDOT films have been intensively studied in respect of the influence of preparation conditions (e.g. [23, 24, 25, 26]), physical and chemical properties [27, 28, 29, 30, 31, 32] as well as analytical and bioanalytical applications [33, 34]. Bobacka et al. [5, 35, 36] have demonstrated that PEDOT films can be successfully applied as a solid contact for polymer-based ISEs, and PEDOT itself is characterized by a linear dependence of the potential vs. the logarithm of the electrolyte ion concentration [5], similar to that of polypyrrole. It was also shown that, in contrast to polypyrrole, PEDOT participates to less extent in side reactions with oxygen and hydrogen ions [33], which can be beneficial from the point of view of interference elimination and application of this polymer as a solid contact.

Although PEDOT has been studied mainly as a transducer layer, less attention has been paid to the properties of this polymer as an ion-sensing membrane. The aim of the present work is to evaluate the possibilities and limits of direct application of highly stable PEDOT films as self-reliant sensing layers, using either a potentiometric or an amperometric mode of ion determination. In this way, we intend to fill the gap between detailed discussions on the electrochemical properties of PEDOT, already present in the literature, and reports on its application as an ion-to-electron transducer. The advantages and disadvantages of this material in comparison to the most often used and studied polypyrrole will be highlighted. Possibilities of obtaining PEDOT films characterized with different ion exchange properties, as well as the interfering influence of redox reactants characterized by relatively fast [Fe(CN)$_6^{3-/4-}$ couple] or slow (O$_2$) electron transfer, will be discussed.

Experimental

Apparatus and materials

Polymerization, voltammetric, chronoamperometric, chronopotentiometric and pulse amperometry experiments were carried out in a conventional one-compartment electrochemical cell with glassy carbon disk electrodes (diameter: 3 or 4 mm) or platinum sheet electrodes (0.5 cm^2, for EDAX measurements), with a Pt counter electrode and a leak-free Ag/AgCl reference electrode in 1 M KCl gel (Mineral, Poland), using an electrochemical analyzer (CHI660, CH Instruments, USA). Open circuit potentiometric measurements made in the two-electrode system were controlled by a multichannel Lawson Labs station M201/M17B EMF recorder (USA), using L-EMF DAQ 2.5 software. The pump systems 700 Dosino

and 711 Liquino (Metrohm, Herisau, Switzerland) were used to obtain sequential dilutions of the calibrating solutions.

The elemental composition of the PEDOT films was determined by energy dispersive analysis of X-rays (EDAX) using a LEO 435 VP electron microscope with Röntec equipment, applying an electron beam energy of 15 keV.

3,4-Ethylenedioxythiophene (EDOT, obtained as Baytron M from Bayer) was used for PEDOT electrosynthesis. All other chemicals were p.a. grade products (Aldrich or Fluka) and were used without further purification. Millipore water was used throughout this work.

Preparation and conditioning of the polymer films

Before EDOT polymerization, the electrodes were polished using Al$_2$O$_3$ (0.3 μm) and were thoroughly washed with water. The polymerization solutions were 6 mM EDOT+electrolyte [KCl (0.1 M) or sodium poly(4-styrenesulfonate) (NaPSS, 0.1 M)] to obtain a polymer film doped by the corresponding anion. Polymerization was carried out galvanostatically by applying an anodic current of 0.2 mA cm^{-2}; the polymerization charge was 0.72 C cm^{-2}, corresponding to a film thickness of 5 μm [30]. Polymer films doped by Fe(CN)$_6^{4-}$ anions [PEDOT(HCF)] were obtained from 6 mM EDOT+0.02 M K$_4$Fe(CN)$_6$ solutions by cycling within the potential range from −0.2 V to 1.1 V with a scan rate of 50 mV s^{-1}. In the latter case, polymerization charges were equal to 0.56, 1.06 or 1.6 C cm^{-2} (approximate thickness: 4, 7.5 and 11.5 μm, respectively [30]). After film deposition the electrodes were rinsed with water and then conditioned overnight in 0.1 M KCl (for potentiometric measurements) or conditioned by cycling in 0.1 M KCl solution, within the range from −0.5 V to 0.5 V, with a scan rate of 50 mV s^{-1} (for other experiments). Electrodes used for EDAX measurements were rinsed just after polymerization and immersed in 0.1 M KCl solutions for 60 s.

All measurements were made at ambient temperature, about 25 °C.

Results and discussion

Potentiometric characteristics of PEDOT films

Figure 1 presents a comparison of the potentiometric characteristics recorded in KCl solutions for PEDOT doped by Cl$^-$ and PSS$^-$ ions (the activities were calculated using Debye–Hückel theory [37]). In the case of PEDOT(Cl), after 24 h conditioning in 0.1 M KCl solution, linear anionic responses were obtained within the range from 10^{-4} M to 1 M with a slope lower than the Nernstian value and a detection limit of 7×10^{-5} M (Table 1). The obtained linear response limit is lower than that observed for polypyrrole doped by chloride ions (∼10^{-4} M) [17]. A significant change of the characteristics during a 6-day period of conditioning of PEDOT(Cl) film (after polymerization) was observed. Although the range of the linear response range was not affected, a systematic decrease of the slope (to −35 mV dec^{-1} after 6 days) was accompanied by only small fluctuations of E^0. This effect is reproducible and is a consequence of a potential decrease for the lowest concentrations and a potential increase for the highest concentrations. In our opinion, the decrease of the slope, indicating a lowering of the permselectivity of the polymer, results from the structure and mechanical

Fig. 1 Potentiometric characteristics of PEDOT(Cl) (*squares*) and PEDOT(PSS) (*triangles*) in KCl solutions
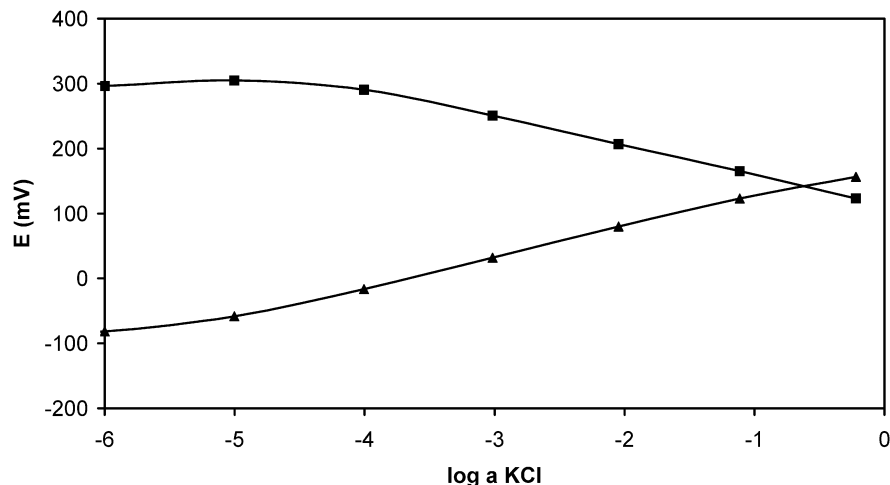
Table 1 Potentiometric characteristics of electrodes modified by PEDOT membranes

Electrode	Slope $\pm$ SD (mV dec^{-1})	$E^0 \pm$ SD (mV)	Detection limit (M)	R^2	Conc. range of linear response (M)
PEDOT(Cl)	-44.4 ± 0.7	115.0 ± 1.8	7×10^{-5}	0.999	10^{-4}–1
PEDOT(PSS)	46.1 ± 1.3	170.8 ± 3.3	3×10^{-6}	0.998	10^{-4}–1
PEDOT(PSS)[a]	46.9 ± 0.9	169.4 ± 3.3	7×10^{-7}	0.998	10^{-6}–1

[a]Potentials recorded under conditions of cathodic polarization using a current density of 3×10^{-7} A cm^{-2}

Table 2 Composition of PEDOT films, expressed in at% of elements (carbon content was not used in calculations), determined using the EDAX method

Polymer	S	Fe	K	Cl
PEDOT(Cl)	24.6	–	0.9	9.0
PEDOT(PSS)	32.9	–	–	–
PEDOT(HCF)	18.8	2.9	0.8	–
PEDOT(HCF), conditioned in 0.1 M KCl for 24 h	21.8	1.2	3.1	1.9

properties of PEDOT(Cl). SEM pictures demonstrate a very loose structure of the film, which can result in penetration of the layer both by anions and cations. Moreover, after prolonged conditioning, PEDOT(Cl) becomes brittle and poorly adhesive to a glassy carbon substrate, giving rise to a decrease in the potentiometric sensitivity. Therefore PEDOT(Cl) films are not a promising material for long-life potentiometric sensors.

For PEDOT(PSS) the slope recorded in the range from 10^{-4} M to 1 M KCl was positive (Table 1), but lower than the theoretical Nernstian value expected for an exclusively cation-exchanging film. However, this value is well comparable with that reported by Bobacka [5]. A similar, cationic and non-selective potentiometric response was earlier obtained for polypyrrole doped by PSS ions [38, 39]. The obtained low value of the slope can be explained by some partial replacement of surface PSS ions by chloride ions during the conditioning. In contrast to PEDOT(Cl), the value of the slope did not change with time, within the limits of experimental error, indicating effective immobilization of bulky dopant ions within the polymer structure. This effect was confirmed by the results of film composition analysis (EDAX), indicating a higher sulfur content compared to

that of PEDOT(Cl) (Table 2). PEDOT(PSS) membranes are characterized by a lower linear response limit (3×10^{-6} M) than observed for polymers doped with Cl$^-$. Moreover, PEDOT(PSS) films are much more stable mechanically than the former polymer, with the SEM picture showing a more dense structure of the polymer. These properties strongly favor PEDOT(PSS) over the Cl$^-$ doped counterpart.

Potentiometric responses of PEDOT(PSS) layers were also studied from the point of view of their selectivity. Table 3 presents slopes and E^0 values of potentiometric characteristics recorded for the same layer of PEDOT(PSS) tested in various electrolyte solutions, in the sequence as given in Table 3. These data show a low influence of the kind of cation (Na$^+$ compared to K$^+$) and anion (Cl$^-$, NO$_3^-$ and SO$_4^{2-}$) on the E^0 value. On the other hand, both anion and cation affect the slope of the potentiometric characteristics. The presented exemplary results confirm the low selectivity and permselectivity of PEDOT(PSS) membranes.

For PEDOT(HCF) films prepared in the presence of bulky Fe(CN)$_6^{3-/4-}$ ions, cationic potentiometric responses, similar to those recorded for PEDOT(PSS), were expected, as observed for polypyrrole doped by

Table 3 Parameters of potentiometric characteristics of PEDOT(PSS) electrodes in different electrolyte solutions (recorded after 2 day conditioning in 0.1 M KCl)

Solution	Slope $\pm$ SD (mV dec^{-1})	$E^0 \pm$ SD (mV)	R^2	Concentration range (M)
NaCl	34.7 $\pm$ 2.6	132.4 $\pm$ 6.5	0.982	10^{-5}–10^{-2}
KNO$_3$	30.2 $\pm$ 1.4	142.9 $\pm$ 3.4	0.993	10^{-4}–10^{-1}
K$_2$SO$_4$	28.8 $\pm$ 0.5	147.5 $\pm$ 1.5	0.999	10^{-4}–10^{-1}
KCl	42.7 $\pm$ 2.3	136.9 $\pm$ 4.4	0.993	10^{-3}–1

Table 4 Dependence of parameters of potentiometric characteristics of PEDOT(HCF) electrodes (polymerization charge: 1.06 C cm^{-2}) on time of conditioning in 0.1 M KCl solution

Conditioning day	Slope $\pm$ SD (mV dec^{-1})	$E^0 \pm$ SD (mV)	R^2
1	-50.9 ± 3.8	167.1 $\pm$ 9.4	0.983
2	-52.8 ± 3.3	186.6 $\pm$ 8.2	0.988
5	-59.9 ± 2.4	175.4 $\pm$ 5.9	0.995
6	-59.3 ± 2.5	170.9 $\pm$ 6.1	0.994
11	-57.8 ± 2.2	155.6 $\pm$ 4.7	0.996

HCF ions [40]. Surprisingly, anionic potentiometric characteristics were obtained, with slopes significantly dependent on the time of conditioning and the film thickness (Table 4). Differently from PEDOT(Cl), the absolute value of the slope increased with time, reaching a Nernstian value after 5 days, for the films of polymerization charge over 1 C cm^{-2}. For thinner films the final value of the slope was slightly lower than the Nernstian value, but its absolute value was higher than 50 mV dec^{-1}. With conditioning, the linear response range was gradually extended to higher concentrations. The value of E^0 did not change significantly.

These data suggest spontaneous exchange of HCF ions by chloride ions during conditioning. This conclusion was confirmed by voltammetric curves of PEDOT(HCF) recorded in 1 M KCl just after polymerizartion and after conditioning in 1 M KCl solutions. A gradual decrease of the anodic and cathodic peaks at potentials near 0.1 V, corresponding to oxidation/reduction of HCF, was observed (Fig. 2), resulting in the disappearance of the peaks after 1 h of open circuit conditioning.

These data enable estimation of the diffusion coefficient of HCF ions in PEDOT film. Assuming semi-infinite diffusion conditions for HCF ions in the polymer at the beginning of the conditioning, the dependence of $Q-Q^0$ on $t^{1/2}$ can be used (Q is the charge obtained by integration of the voltammetric peak corresponding to HCF oxidation or reduction after conditioning time t; Q^0 is this charge recorded for the film just after polymerization). The slope of this dependence (Fig. 3) is assumed to be $2FD^{1/2}Ac/\pi^{1/2}$, where A is the electrode surface area and c is the concentration of HCF forms in the film, calculated using the equation:

$$c = \frac{Q^0}{FAd} \tag{1}$$

for known values of the film thickness, d.

The diffusion coefficient can be also estimated from the equation:

$$D = \frac{d^2}{\tau} \tag{2}$$
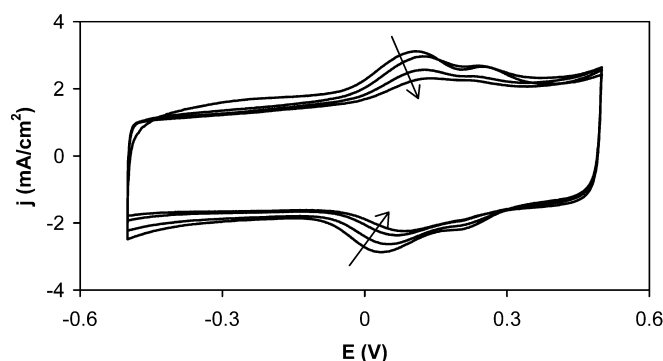
Fig. 2 Voltammetric curves of PEDOT(HCF) (polymerization charge: 1.6 C cm^{-2}) in 1 M KCl, after 0 (just after polymerization), 100, 500 and 1200 s open circuit conditioning in 1 M KCl solution. Scan rate 50 mV s^{-1}

where τ is conditioning time after which the HCF oxidation/reduction peaks disappear. Both methods give consistent results, $D = 3 \times 10^{-10}$ cm^2 s^{-1}, two orders of magnitude lower than recorded for Cl$^-$ ions [30].

Elemental analysis of PEDOT(HCF) layers using EDAX confirmed the occurrence of the exchange process of HCF by Cl$^-$ anions and the low rate of this process (Table 2). Just after polymerization the film contained almost 3 at% Fe and the presence of Cl in the film was not detected. After 24 h conditioning in 0.1 M KCl the amount of Fe decreased to 1.2%. Moreover, almost 2 at% Cl was detected. Therefore, after long conditioning, PEDOT(HCF) became an anion exchanger containing dopant chloride ions. The properties of this film differ significantly from those of PEDOT(Cl) polymerized in the presence of chloride ions, although it is now also doped by chloride ions. The initial presence of bulky HCF ions incorporated in the course of polymerization makes the structure more ordered (as confirmed by SEM pictures; not presented) and stable mechanically. As a result, the value of the slope of the potentiometric characteristics does not decrease in time. Therefore, this polymer is more promising as a membrane for an anionic potentiometric sensor than PEDOT(Cl) itself.

Fig. 3 Dependence of $Q-Q^0$ on $t^{1/2}$ (see text) obtained from voltammetric curves of PEDOT(HCF) (polymerization charge: 1.6 C cm^{-2}) in 1 M KCl. Electrode surface area 0.125 cm^2
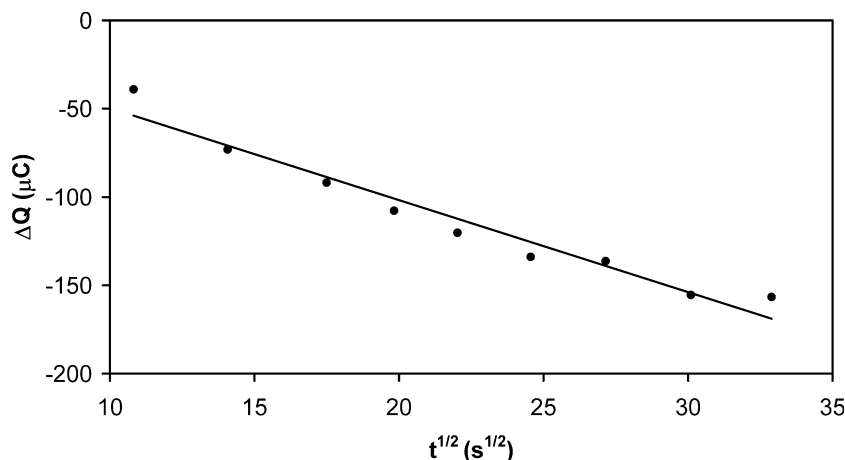
Fig. 4 Potentiometric characteristics of PEDOT(PSS) in KCl solutions containing the redox couple Fe(CN)$_6^{3-/4-}$ (potassium salts of equal concentrations): 0 (*diamonds*), 10^{-5} (*squares*), 10^{-4} (*triangles*), 10^{-3} (*crosses*), 10^{-2} M (*circles*)
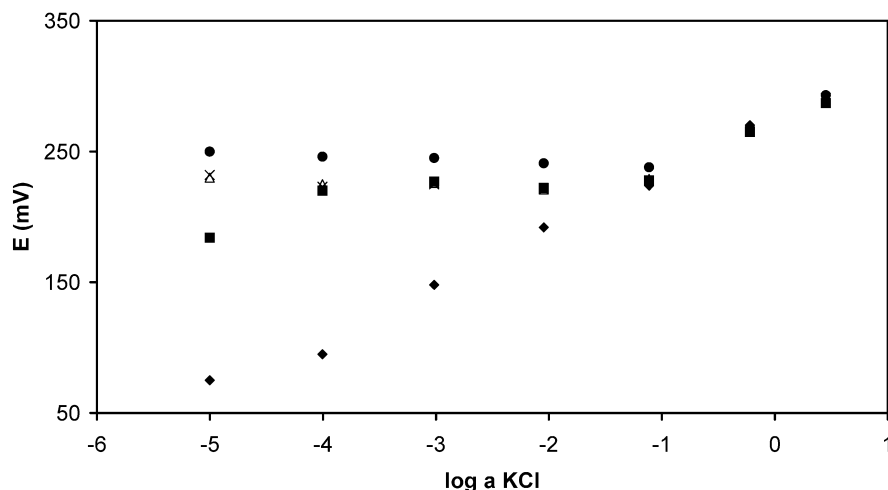
Redox interferences

PEDOT films are both electronically conductive and able to participate in redox processes; therefore the potential of a PEDOT membrane can be (as for other conducting polymer films) affected by the presence of redox reactants in the sample solution. This effect is often the critical issue from the practical point of view, owing to the common presence of redox reactants, e.g. dissolved oxygen.

Recently, it was shown that the influence of redox reactants on the potentiometric responses of conducting polymers was highly dependent on the rate of the charge transfer reaction between the redox species and the conducting polymer [41]. Therefore, in this work the influence of redox reactants on the potentiometric characteristics of PEDOT films was examined for reactants characterized both by a low charge transfer rate (dissolved oxygen) as well as by a relatively high one [Fe(CN)$_6^{3-/4-}$].

The influence of oxygen was checked by recording the potentiometric characteristics in solutions containing dissolved oxygen and solutions purged with argon. As

oxygen was gradually removed, the potential slowly shifted towards lower values and after 4 h of purging a stable potential value was obtained. Potentiometric characteristics obtained for PEDOT(PSS) recorded in KCl solution, and in the absence and presence of dissolved oxygen, are characterized with similar slopes, within the limits of experimental error. The same result was obtained for PEDOT(Cl) (the same slopes in the absence and presence of oxygen). Lines recorded in de-aerated solutions are shifted by ca. 0.2 V to lower potentials. A similar effect was recorded earlier for polypyrrole electrodes [41].

Figure 4 illustrates the influence of the redox couple Fe(CN)$_6^{3-/4-}$ on the potentiometric characteristics of PEDOT films. Potentiometric characteristics in KCl solutions in the range from 10^{-5} M to 1 M were recorded for variable concentrations of the Fe(CN)$_6^{3-/4-}$ couple (equal concentrations of both forms). The redox couple concentration was constant throughout the recording of the open circuit potential on the logarithm of the KCl concentration. The results presented for PEDOT(PSS) show that even for a redox couple concentration as low as 10^{-5} M the potential dependence on

log[KCl] practically disappears, with the resulting potential becoming equal to the redox potential of the $Fe(CN)_6^{3-/4-}$ couple, indicating an extremely high redox susceptibility of PEDOT(PSS). Analogous dependences were obtained for PEDOT(Cl) (results not shown). This result is essentially different from that recorded for polypyrrole electrodes, for which the potential is more resistant towards the influence of this redox couple [41], and the effect equal to that recorded for PEDOT was observed at 10^{-3} M $Fe(CN)_6^{3-/4-}$ concentration.

These quite different susceptibilities towards redox interferences (higher for PEDOT compared to polypyrrole) can be ascribed to a different extent of the spontaneous processes of polymer charging and discharging, represented by oxidation by oxygen [42] or deprotonation of oxidized polypyrrole [43, 44], respectively. Under open circuit conditions the sum of the oxidation currents flowing across the polymer/solution interface is equal to the sum of the reduction currents:

$$i_{charg} + i_{red} = i_{discharg} + i_{ox} \qquad (3)$$

where i_{charg} and $i_{discharg}$ are currents corresponding to spontaneous charging and discharging, respectively, while i_{ox} and i_{red} are oxidation and reduction currents of the $Fe(CN)_6^{3-/4-}$ couple, respectively. In the case of polypyrrole, the charging and discharging currents are relatively high, in the range of μA cm^{-2} [43]; thus the addition of redox reactant (resulting in appearance of i_{red} and i_{ox}) does not change significantly the measured potential, if the redox reactants concentration is not high. The spontaneous processes of charging/discharging exert a leveling effect (a quantitative discussion of this influence for polypyrrole is presented elsewhere [41]). On the other hand, for PEDOT films the role of the spontaneous charging/discharging phenomena is very low, and the currents i_{charg} and $i_{discharg}$ are comparable to those recorded for a bare substrate electrode [45]. Therefore, PEDOT films are much more sensitive towards the addition of redox interferents of a given concentration (giving rise to i_{ox} and i_{red} values) compared to polypyrrole.

For a reactant of low charge transfer rate (as O_2), the current corresponding to this reactant flows practically only in one direction (reduction of O_2), giving rise to the increase of the current on the left hand side of Eq. 3. As a consequence, the open circuit potential moves towards higher values.

Lowering the potentiometric detection limit of PEDOT films

The detection limit of PEDOT membranes is near 10^{-5} M under open circuit conditions (Table 1). Similarly as for polypyrrole, it results from the leakage of electrolyte anions or cations (in the case of anion- and cation-exchanging membranes, respectively) from the film into the solution layer adjacent to the polymer/solution interface. The source of this effect can be either spontaneous charging/discharging of the polymer [43] or an ion concentration gradient between the polymer membrane (containing pre-concentrated ions during polymerization and conditioning steps conducted at higher concentration) and the dilute sample solution. In the case of a conducting polymer membrane, this sample-oriented ion flux can be diminished by applying a small current in order to compensate for the ion leakage from the polymer into the sample. This method has been successfully used to lower the detection limit of typical solvent polymeric membrane ion-selective electrodes [46, 47, 48] as well as polypyrrole film electrodes [49].

The effect of galvanostatic polarization on the potentiometric characteristics was checked for PEDOT(PSS) films. Calibration lines for the potential vs. log$a(K^+)$ in KCl were recorded within the range of KCl concentrations from 10^{-8} M to 1 M, applying small anodic or cathodic current densities, compared to currents corresponding to bulk polymer oxidation/reduction. The optimal density of the cathodic current is equal to 3×10^{-7} A cm^{-2}, resulting in a detection limit of 7×10^{-7} M, with the slope and E^0 equal, within the limits of experimental error, to those recorded under zero-current conditions (Table 1) and with a potential drift lower than 1 mV min^{-1}. It should be underlined that for poorly selective PEDOT(PSS) films the detection limit cannot be lower than 10^{-7} M, since the minimal total cation concentration in aqueous solutions is limited by this value. The improvement of the characteristics is observed for a cathodic polarizing current since it favors cation incorporation into the membrane, resulting in elimination of the effects of cation leakage from the polymer into the solution layer near the polymer surface.

An anodic current causes a reverse effect, i.e. an increase of the detection limit, compared to zero-current conditions, owing to cation release from the membrane into the adjacent solution layer.

It should be noted that the polarizing current needed to decrease the detection limit is about 10-fold lower than in the case of polypyrrole [49], in our opinion due to the low rate of the spontaneous discharge process in the case of PEDOT(PSS) and the low concentration of mobile ions in this film. The low value of the polarizing current favors PEDOT over polypyrrole, because for a lower current certain perturbations, e.g. connected with the possible influence of (1) uncompensated solution resistance and (2) oxidation/reduction of the polymer, are less severe. Taking into account the uncompensated resistance of the solution with a KCl concentration lower than 10^{-4} M (determined using electrochemical impedance spectroscopy and by extrapolating the recorded impedance to very high frequencies [49]), the estimated ohmic potential drop for the highest polarizing current is in the range of single millivolts. On the other hand, the charge of polymer reduction during measurement (3×10^{-7} A cm$^{-2} \times 0.07$ cm$^2 \times 200$ s) is below 5 μC, i.e. below 0.2% of the charge accumulated in the partly oxidized PEDOT, estimated by integration of the voltammetric curves. Therefore, both mentioned effects

Fig. 5 Chronoamperometric curves of PEDOT(PSS) reduction (starting potential: 0.5 V; final potential: −0.5 V) for longer (**A**) and shorter (**B**) times after potential step application. Electrode surface area 0.07 cm^2
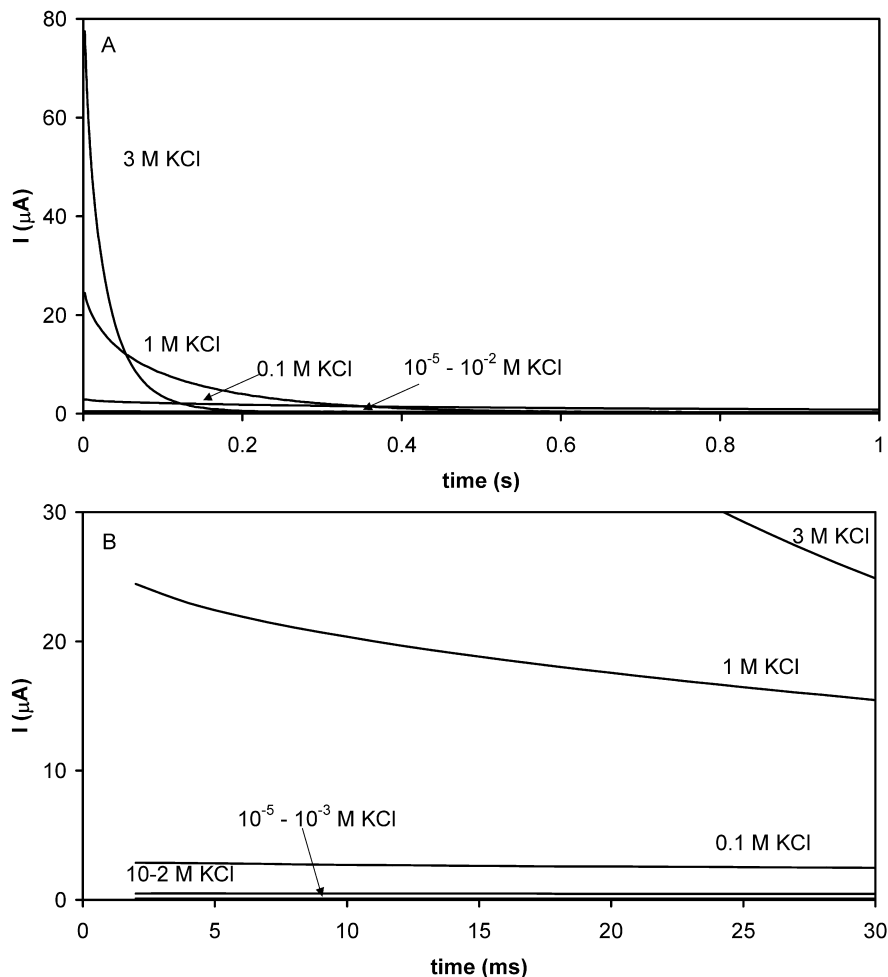
exert negligible influence on the potentiometric characteristics of PEDOT films.

## Amperometric characteristics of PEDOT films

Ion-sensing properties of conducting polymer membranes can be explored not only under potentiometric but also under amperometric conditions. The latter mode seems to be more advantageous from the point of view of interference elimination, e.g. by choosing the appropriate electrode potential. Upon oxidation (reduction) of the anion (cation) exchanging polymer, incorporation of anions (cations) into the membrane is expected. The current recorded should increase with the increasing concentration of anions (cations) in solution, for an anion (cation) exchanging film, respectively.

Figure 5A presents typical chronoamperometric curves of PEDOT(PSS) reduction in KCl solutions of different concentrations [analogous results were obtained for PEDOT(Cl), representing an oxidation process]. One can observe a rapid decrease of the current and a non-monotonous dependence of the current on electrolyte concentration for times longer than 50 ms. A

relation of this type has no analytical value owing to the current change and the lack of concentration dependence for longer times; however, it is usually observed for conducting polymers, e.g. [22].

This shape of the dependence results from two kinds of system response [22, 50]. For very short times the current is limited both by uncompensated solution resistance and ion transport in the polymer film. In this time range the current is dependent on ion concentration in the solution. The effect of uncompensated resistance of the solution is pronounced for a much longer time than for a bare metal electrode (milliseconds compared to microseconds for a bare electrode after potential step application), owing to the high capacity of the polymer film. For longer times the oxidation (reduction) process is nearly completed and a low current is recorded, dependent on the properties of the polymer film. For this time domain the solution concentration exerts a minor influence on the flowing current. Our recent work concerning the application of polypyrrole membranes [22] showed that the highest sensitivity and an extended linear range of response can be obtained if the pulse polarization mode is used and current measurement is just after the potential step application in the range 20–500 ms.

Fig. 6 Pulse amperometric characteristics of PEDOT(Cl) (**A**) and PEDOT(PSS) (**B**) in KCl solutions containing the redox couple $Fe(CN)_6^{3-/4-}$ (potassium salts of equal concentrations): 0 (*crosses*), 10^{-5} (*squares*), 10^{-4} (*triangles*), 10^{-3} (*circles*), 10^{-2} M (*diamonds*). Potential step: from -0.5 V to 0.5 V (**A**) or from 0.5 V to -0.5 V (**B**); pulse duration time 10 ms; electrode surface area 0.07 cm^2
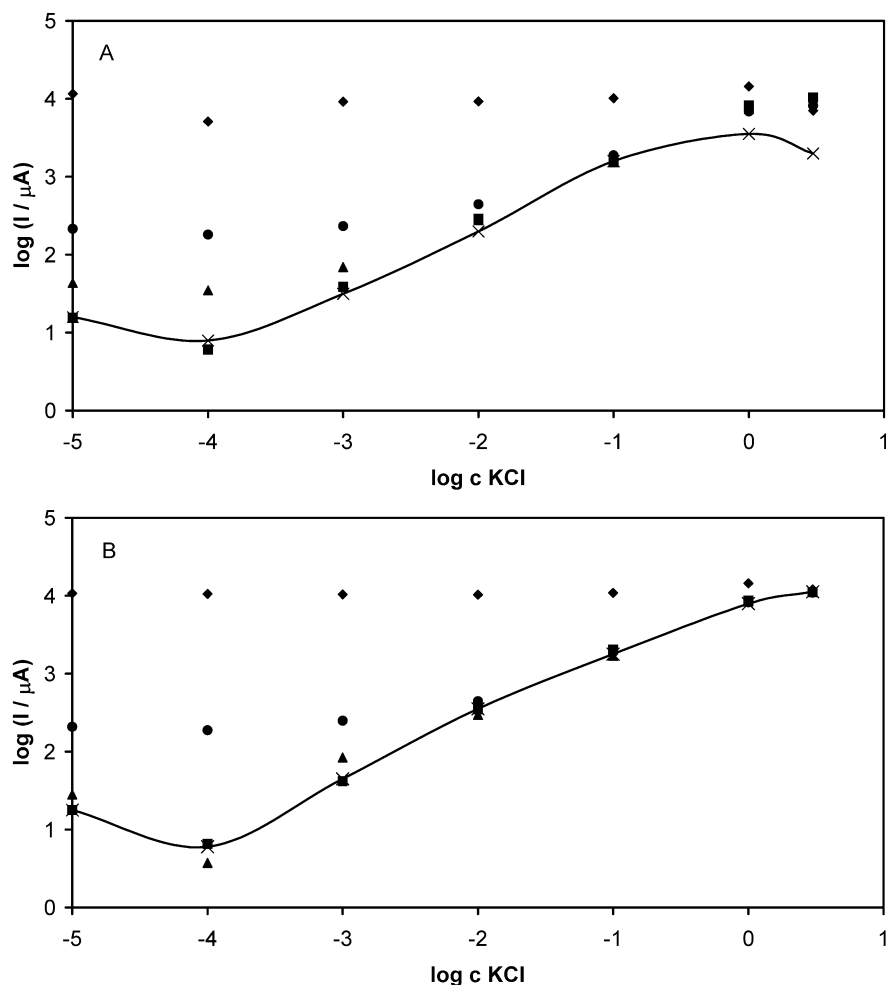
Therefore, in the following experiments the current dependence on electrolyte concentration was studied for short times (up to 30 ms). Figure 5B shows that the current recorded in this time range is almost constant (for lower electrolyte concentrations) and significantly dependent on KCl concentration.

The results of pulse amperometric measurements are presented in Fig. 6 in the form of dependences of the logarithm of the current on the logarithm of the KCl concentration for a given pulse potential [change of potential from -0.5 V to 0.5 V and from 0.5 V to -0.5 V for PEDOT(Cl) and PEDOT(PSS), respectively; pulse time 10 ms]. A linear dependence is observed within the concentration range from 10^{-4} M to 1 M, i.e. within the range comparable to that obtained using potentiometry. The logarithmic scale was used to cover the wide range of electrolyte concentration changes. The slope of the amperometric characteristics is 0.69 ± 0.04 and 0.79 ± 0.02 for PEDOT(Cl) and PEDOT(PSS), respectively, lower than 1.0 expected for a linear dependence of current versus analyte concentration. These results demonstrate that a simple arrangement as well as a facile and cheap procedure for film preparation enables obtaining amperometric sensors for non-electroactive ions, within an applied potential range, operating in the concentration range of ion-selective electrodes.

In the next step the interfering influence of redox reactants on amperometric characteristics was checked. The plots of log(current) versus log(KCl concentration) recorded in the absence and presence of dissolved oxygen were identical within the limits of experimental error (results not shown), indicating a negligible role of oxygen as a redox interferent. This result strongly favors the amperometric method over the potentiometric one, where a significant influence of oxygen concentration on the potential value (the slope of the characteristics was unchanged) was observed.

Figure 6 presents the influence of the $Fe(CN)_6^{3-/4-}$ couple of different concentrations on the amperometric characteristics of PEDOT(Cl) (Fig. 6A) and PEDOT(PSS) (Fig. 6B) films (equal concentrations of the oxidized and reduced forms). In contrast to the potentiometric mode of sensing, for the redox couple concentrations of 10^{-5} M and 10^{-4} M, only a slight influence on the response was recorded. An increase in $Fe(CN)_6^{3-/4-}$ concentration leads to a narrowing of the linear range of the response and increase of the detection limit (this detection limit is fairly close to redox couple concentration). This influence can result from oxidation

(reduction) of the redox reactant and possible participation of $Fe(CN)_6^{3-/4-}$ and K^+ ions in charge compensation of the polymer. This interfering influence is almost independent of the ion exchange properties of the polymer film. The obtained results correspond well to the interfering effect of $Fe(CN)_6^{3-/4-}$ on the pulse amperometric characteristics of polypyrrole [22].

Conclusions

PEDOT films obtained by electropolymerization can be used as active membranes for either potentiometric or amperometric ion sensors. For both measurement modes tested the range of linear responses is similar, exceeding four orders of magnitude for KCl solutions. The potentiometric detection limit for PEDOT(PSS) can be lowered to reach the range of 10^{-7} M under conditions of polarization with a relatively low cathodic current, owing to prevention of cation leakage from the polymer film into the sample solution. The influence of redox interferents in potentiometry can be interpreted in terms of parallel charge transfer processes: spontaneous charging/discharging of the polymer and redox processes of the interferent. Thus, a crucial role of charge transfer kinetics was confirmed: only interferents characterized by a high charge transfer rate constant significantly suppress the potentiometric responses.

Summarizing, the potentiometric method offers a wider accessible concentration range (especially when using a small polarizing current) but the pulse amperometric method, with a less extended concentration range, is favored from the point of view of interference elimination and a simpler sensor preparation procedure (no need for long conditioning). Both methods suffer from low selectivity, related to the conducting polymer material property; therefore they can be used after an ion separation step, e.g. using chromatography.

For electrochemical ion sensing, PEDOT membranes are favored over polypyrrole layers owing to higher stability, less severe pH influence [33] and a better potentiometric detection limit, as well as a lower current needed to decrease the detection limit under conditions of polarized electrode potentiometry.

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