Interfering Influence of Redox Reactants on Potentiometric Responses of Electrodes with Conducting Polymer Films

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Conducting polymer (CP) films, used as ion-sensing membranes under open-circuit potentiometric conditions, are highly sensitive towards redox interferents, which seriously limit their analytical application. The factors affecting potential transients upon addition of redox reactant, as well as stable potentiometric responses in the presence of selected model redox reactants have been considered. The role of polymer redox capacitance and charge transfer kinetics has been studied. Theoretical predictions and experimental results obtained for polypyrrole, poly(N-methylpyrrole), and poly(3,4-ethylenedioxythiophene) (PEDOT) in the presence of Fe(CN)$_6^{3-/4-}$ confirm a crucial role of spontaneous charging and discharging processes of CP films (e.g. polymer oxidation by dissolved oxygen, or deprotonation) for redox sensitivity. An experimental protocol utilising polarized electrode potentiometry has been developed in order to determine charging/discharging currents of the polymer in the absence and presence of added redox reactants. Polymers characterized by a significant charging/discharging rate (e.g. polypyrrole doped with perchlorate ions) have been found more resistant towards redox interferences than more stable polymers (e.g. PEDOT) with low-rate charging/discharging. This effect can be of a key importance not only for the CP-based ion-sensitive membranes, but also for conducting polymers used as ion-to-electron transducers (solid contacts) in all-solid-state ion-selective electrodes.

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Warstwy polimerów przewodzących, stosowane jako membrany jonoczule w warunkach potencjometrycznych, są bardzo podatne na wpływ interferentów redoks, silnie ograniczając ich zastosowania analityczne. W pracy rozpatrywano czynniki wpływające zarówno na zmiany potencjału w czasie po dodaniu reagenta redoks, jak i stabilne odpowiedzi potencjometryczne rejestrowane w obecności wybranych modelowych reagentów redoks. Dyskutowano również rolę pojemności reaksu i kinetyki przeniesienia ładunku. Przewidywania teoretyczne i wyniki eksperymentalne uzyskane dla polipiriolu, poli(N-metylopirolu) i poli(3,4-etylenodioksytiofenu) (PEDOT) w obecności układu Fe(CN)$_6^{3–/4–}$ potwierdziły kluczową rolę samorzutnych procesów ładowania i rozładowania polimerów przewodzących (jak np. utlenianie polipiriolu tlenem z roztworu lub deprotonowanie) dla czułości redoks.

Opracowano procedurę eksperymentalną, wykorzystującą potencjometrię z elektrodami polaryzowanymi, w celu wyznaczania prądów związanych z ładowaniem/rozładowaniem polipiriolu w nieobecności i obecności dodanego reagenta redoks. Wykazano, że polimery charakteryzujące się dużą szybkością procesu ładowania/rozładowania (jak polipiriol domieszkowany jonami chloranowymi(VII)) są odporniejsze na interferencje redoks niż bardziej trwałe polimery (jak np. PEDOT) charakteryzujące się małą szybkością ładowania/rozładowania. Efekt ten ma kluczowe znaczenie nie tylko dla polimerów przewodzących pełniących rolę membrany jonoczulej, ale też dla polimerów stosowanych jako przetworniki jonowo-elektronowe (stałe kontakty) w elektrodach jonoselektywnych pozbawionych roztworu wewnętrznych.

Conducting polymer (CP) films are materials of unique properties, which make them interesting for diverse applications. Coupled electronic and ionic conductivity, reversible doping, as well as the dependence of physical and chemical properties on the oxidation state are desirable for the construction of the sensor with facile chemical-to-electrical signal transduction. Potential applications of conducting polymers in amperometric (voltammetric) [1, 2] and potentiometric, e.g. [3–10] ion sensors, have been widely studied. These polymers have been applied as membrane materials in the construction of conducting polymer – based ion-selective electrodes (see [3, 11–17], and recent reviews [18, 19]). Preparation of the sensor is simple and fast, and potentiometric responses of CP can be relatively simply tailored: the films electrodeposited in the presence of small, easily exchangeable anions are characterised with anion-sensitivity, whereas those prepared from monomer solutions containing bulky anions usually give cationic potentiometric responses [3, 11–17]. The linear response range is limited to the activities from 1 mol L$^{-1}$ to $10^{–4}$–$10^{–5}$ mol L$^{-1}$, being reasonable for typical applications [3, 4, 11–17]. Severe interferences are caused by other ions present in the solution and are due to low selectivity and permselectivity of conducting polymer films, as well as to the protonation of the polymer in acidic solutions [20–25].

However, the most severe interferents are redox reactants present in the sample. In the presence of either oxidizing or reducing agents, polymer may undergo redox transformation resulting in the change of the open-circuit potential. Therefore, these reactants highly affect analytical dependences of the potential on the logarithm of activity of the electrolyte ion. Even for relatively low concentration of redox couple,
the polymer open-circuit potential may reflect only the solution redox potential, being independent of the changes of electrolyte ions’ concentration [24]. For instance, for polypyrrole – modified electrodes this effect is observed in the presence of 1 mmol L$^{-1}$ Fe(CN)$_6^{3-/4-}$ – a typical redox couple. The influence of redox reactants on CP potentiometry has been a subject of theoretical description and model calculations [24, 26].

The interfering effect is reflected not only in the final potential value, but also in the potential transient, before the final value is reached. It has been demonstrated that the rate of potential changes upon contact with redox reactants depends on ion-exchange properties of the CP membranes [27]. For polypyrrole films doped with Cl$^-$ ions (facile ion exchange), the time needed to obtain a stable potential was long (above 10 min), while for polypyrrole doped with dodecylsulphate ions (limited ion exchange) an instantaneous, metallic-like response was obtained [27].

Recently, we have shown that the redox response of polypyrrole films is strongly affected by spontaneous charging/discharging of the polymer [19, 24, 28]. The oxidised polymer film may undergo spontaneous discharge, e.g. due to deprotonation [29]. In contrast, the reduced polymer can be spontaneously oxidised, e.g. by dissolved oxygen [30, 31]. These processes are connected with ion exchange between the polymer and the solution, compensating the resulting charge changes. To confirm the role of charging/discharging processes for redox responses, it is advisable to carry out such studies also for other conducting polymers.

The aim of this paper is to summarize the factors that disturb redox responses of CP films by affecting (i) potential transient and (ii) final stable values. In case (i), the obtained results are compared with theoretical predictions of the rate-determining step. In case (ii), the influence of spontaneous charging/discharging is studied for several polymers of different ion exchange properties: polypyrrole, poly(N-methylpyrrole), and poly(3,4-ethylenedioxythiophene). An experimental procedure to determine the rate of these processes has been proposed. Based on the results, we propose methods helpful to eliminate, or at least to diminish, the interference of redox reactions in CP-based potentiometric ion sensors. The results obtained herein might be useful for the construction of redox interference – free all-solid-state ion-selective electrodes with CP ion-to-electron transducers.

**EXPERIMENTAL**

**Reagents**

Distilled pyrrole and N-methylpyrrole were stored in a refrigerator and prior to the use they were purified by passing through a home-made alumina gel mini-column. 3,4-ethylenedioxythiophene monomer was stored in a refrigerator and used as received.
Doubly distilled and freshly deionised water (resistance 18.2 MΩcm, Milli-Qplus, Millipore, Austria) was used throughout. The salts used were of analytical grade. Mean ion activities were calculated according to Debye–Hückel theory [32].

**Apparatus and electrodes**

A multi-channel data acquisition setup and software (Lawson Labs Inc., 3217 Phoenixville Pike, Malvern, PA 19355, USA) were used in the open-circuit potentiometric experiments. In other electrochemical measurements, a CH galvanostat-potentiostat, model 660 A (CH–Instruments, Austin, TX, USA) was utilised.

A double junction silver/silver chloride reference electrode with the outer compartment filled with 1 mol L$^{-1}$ lithium acetate (Möller Glasbläserei, Zürich, Switzerland) was used.

Platinum foil of the area of 2 cm$^2$ served as a counter electrode. Glassy carbon disc electrodes (area: 0.07 cm$^2$) were polished with Al$_2$O$_3$, 0.3 mm.

The measured open-circuit potential values, after correction for the liquid junction potential drop (calculated according to the Henderson’s approximation), were used to construct the calibration plots. Potential values recorded in galvanostatic experiments were corrected for the ohmic drop. The latter was calculated by multiplying the applied current value by the solution resistance determined for each concentration in electrochemical impedance spectroscopy experiments (frequency range: 1 Hz –100 kHz, amplitude: 10 mV), and extrapolating the results to extremely high frequencies. The calculated ohmic drop was then subtracted from the potential values recorded under galvanostatic conditions in potential vs time measurements.

**Preparation of conducting polymer films**

Conducting polymer films were obtained in the course of electrochemical deposition from one of the following aqueous solutions: 0.2 mol L$^{-1}$ pyrrole and 0.1 mol L$^{-1}$ NaClO$_4$ to yield poly(pyrrole) doped with perchlorate – PPyClO$_4$; 0.2 mol L$^{-1}$ pyrrole and 0.1 mol L$^{-1}$ KCl to yield poly(pyrrole) doped with chloride – PPyCl; 0.1 mol L$^{-1}$ pyrrole and 0.5 mol L$^{-1}$ K$_4$Fe(CN)$_6$ to yield poly(pyrrole) doped with hexacyanoferrate anions – PPyFeCN; 0.1 mol L$^{-1}$ N-methylpyrrole and 0.1 mol L$^{-1}$ sodium poly(4-styrenesulfonate) anions to yield poly(N-methylpyrrole) doped with poly(4-styrenesulfonate) anions – PMPyPSS; 6 × 10$^{-3}$ mol dm$^{-3}$ 3,4-ethylenedioxythiophene and 0.1 mol dm$^{-3}$ sodium poly(4-styrenesulfonate) to obtain poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonate) anions – PEDOT-PSS. Poly(pyrrole) layers were electrodeposited potentiostatically at 0.9 V, the polymerization charge (if not stated otherwise) was 1.43 C cm$^{-2}$ for PPyClO$_4$ and 2.15 C cm$^{-2}$ for PPyFeCN (in the latter case 1/3 of the polymerization charge is consumed in the oxidation of the doping anion [33]). Poly(N-methylpyrrole) was polymerized potentiostatically at 0.7 V, the polymerization charge was 1.07 C cm$^{-2}$. PEDOT-PSS films were obtained galvanostatically by passing the current of 0.2 mA cm$^{-2}$ for 60 min; the polymerization charge was 0.72 C cm$^{-2}$. The approximate thickness of all polymer films was 3–10 mm, depending on the polymerization charge [34, 35].

After polymerization, the obtained films were thoroughly rinsed with deionised water and transferred to 0.1 mol L$^{-1}$ KCl (PPyCl, PPyFeCN, PEDOT-PSS) or 0.1 mol L$^{-1}$ NaClO$_4$ (PPyClO$_4$) solution, alternatively to 0.1 mol L$^{-1}$ sodium poly(4-styrenesulfonate), NaPSS, (PMPyPSS) solution, and were polarized under conditions of cyclic voltammetry (potential range from –0.5 to 0.5 V, scan rate: 50 mV s$^{-1}$, 3 scans). Then, the films were conditioned overnight in 0.1 mol L$^{-1}$ KCl (PPyCl, PPyFeCN, PEDOT-PSS), 0.1 mol L$^{-1}$ NaClO$_4$ (PPyClO$_4$), or in 0.1 mol L$^{-1}$ NaPSS (PMPyPSS) solution. The PMPyPSS film was conditioned in 0.1 mol L$^{-1}$ KCl solution for 1 h directly before measurements.
Interfering influence of redox reactants on potentiometric responses

Determination of the charge flow rate under open - circuit conditions

Conducting polymer films, after conditioning, were transferred to $10^{-4}$ mol L$^{-1}$ KCl (or NaClO$_4$ in the case of PPyClO$_4$), or to the same solution spiked with the potassium salt of the redox reactant: Fe(CN)$_6^{4-}$ or Fe(CN)$_6^{3-}$. Anodic and cathodic currents were applied alternatively for 180 s ($3 \times 10^{-8}$ A, $5 \times 10^{-8}$ A, $8 \times 10^{-8}$ A for PPyFeCN, PPyPSS and PEDOT-PSS and $1 \times 10^{-7}$ A, $3 \times 10^{-7}$ A, $5 \times 10^{-7}$ A for PPyClO$_4$), and open-circuit potentials were also recorded.

The potential changes recorded under either open-circuit or galvanostatic conditions were used to estimate the charge flow under open-circuit conditions.

Theoretical considerations

Discussing the influence of redox interferents on potentiometric characteristics of CP membranes, two important issues should be addressed: open-circuit potential transient upon the contact with the redox reactant („kinetic” effect), and the established final potential value („steady state” effect). These two effects have been partly discussed in the previous works, e.g. [24, 26, 27], however, some supplement to this topic is needed.

Potential transients

The rate of potential changes of CP films under the influence of redox reactant depends on different factors, such as: reactant’s concentration, reactant’s transport rate in the solution, charge transfer kinetics, film thickness, concentration of ion-exchanging sites in the polymer, and kinetics of ion exchange at the polymer/solution interface. Taking into account the properties of the polymer film, i.e. charge transfer kinetics and redox capacitance (dependent on the film thickness and related to the oxidation/reduction and ion-exchange properties), various limiting cases can be distinguished.

Case 1. High redox capacitance, high charge transfer rate. The redox reaction between the polymer and the redox reactant is fast and the overall rate of the process is controlled by the reactant’s transport rate in the solution. Even for high concentration of the redox reactant, when a significant amount of charge is transferred across the polymer/solution interface, the corresponding potential changes are rather slow, owing to high redox capacitance of the polymer. Consequently, the rate of the potential change is low and depends on the solution stirring. In the absence of stirring and assuming purely diffusive transport, the charge $\Delta q$, flowing across the polymer/solution interface and accompanying redox transformation of the polymer, can be described by the integrated form of the Cottrell’s equation:

$$\Delta q = \frac{2FAe(Dt)^{1/2}}{\pi^{1/2}}$$  \hspace{1cm} (1)
where $A$ is electrode surface area, $F$ is Faraday constant, $D$ and $c$ are diffusion coefficient and concentration of redox reactant in the solution, $t$ is time elapsed after immersion to the solution containing the redox component. Then, $\Delta q$ can be recalculated to the open-circuit potential change, $\Delta E_{OCP}$, using the following relation:

$$\Delta E_{OCP} = \frac{\Delta q}{C}$$

(2)

where $C$ is the low-frequency (redox) capacitance of the polymer film. Then, assuming that $C$ is independent of the potential (practically fulfilled for the oxidized polypyrrole), the time dependence of the open-circuit potential is described by the formula:

$$\Delta E_{OCP} = \frac{2FAC(Dt)^{1/2}}{\pi^{3/2}C}$$

(3)

**Case 2. High redox capacitance, low charge transfer rate.** Charge transfer is the rate determining step resulting in a small charge flowing across the interface for a given period of time. Due to high capacitance and relatively small charge exchanged, the rate of the potential change is lower than in case 1; in extreme cases the potential of the CP electrode is rather insensitive to the presence of the redox reactant. The highest value of the charge transfer rate constant, for which the redox reactant does not affect the open-circuit potentiometric response, can be easily estimated. Assuming the tolerable potential drift of 0.1 mV min$^{-1}$ upon the influence of redox interferent, the allowed flowing charge $\Delta q$ can be calculated from equation 2. Then, assuming the time-independent rate of one electron charge transfer process, $\Delta E_{OCP}$ can be related to the rate constant:

$$\Delta E_{OCP} = \frac{FAckt}{C}$$

(4)

For typical values: $c = 1$ mmol L$^{-1}$, $A = 0.07$ cm$^2$ and $C = 10$ mF, the highest allowed rate constant that fulfils the above condition of potential stability (0.1 mV min$^{-1}$) is $k \sim 10^{-6}$ cm s$^{-1}$.

**Case 3. Low redox capacitance, high charge transfer rate.** Since the amount of the flowing charge is high and the capacitance is low, the potential is altered instantaneously, in extreme case similarly as for conventional metal electrode.
Case 4. Low capacity, low charge transfer rate. Different potential vs time relations can be observed, depending on relative values of parameters.

Final potentials. Influence of spontaneous processes of CP

After reaching final stable potential, the polymer film can still undergo some spontaneous charging/discharging, described elsewhere [24, 28, 36, 37]. These processes can be typical redox reactions, as e.g. oxidation by oxygen in the solution (resulting in potential increase), and other processes, e.g. polymer deprotonation accompanied by potential drop. If the rate of potential increase (charging) is equal to that of potential decrease (discharging), then stable potential is measured.

The above mentioned processes are accompanied by the ion flow between the polymer film and the solution. The potential increase processes are coupled with either cation release from the polymer, or anion incorporation. For potential – decreasing reactions, a reversed flow is observed. Typically, in relatively concentrated solutions, potential decrease and potential increase processes compensate mutually [37].

However, in dilute solutions the processes accompanied by ion flow from the polymer to the solution are preferred, e.g. oxidation of cation-exchanging polymer is coupled with the release of cations. Imbalanced charging/discharging processes result in potential drift in dilute solutions; then, the following equation holds [37]:

$$\frac{\Delta E_{OCP}}{\Delta t} = \frac{i_b}{C}$$

(5)

where $\Delta E_{OCP}$ is the open-circuit potential change for a time period $\Delta t$; $i_b$ current relates to the interfacial charge flow, e.g. between the oxidizing agent and the polymer. $i_b$ current can be obtained applying an external current, $i_{appl}$ and comparing the recorded potential drift $\Delta E$ with $\Delta E_{OCP}$ [37]. Potential drift in the presence of $i_{appl}$ (under conditions of polarized electrode potentiometry) is described by the following formula (attributing the positive sign for anodic current):

$$\frac{\Delta E}{\Delta t} = \frac{i_{appl} + i_b}{C}$$

(6)

Combining equations 5 and 6, and after rearrangement, one obtains [37]:

$$i_b = \frac{\Delta E_{OCP}}{\Delta E - \Delta E_{OCP}} \cdot i_{appl}$$

(7)

Equation 7 can be used to calculate $i_b$ values and to compare the numbers measured in the absence and in the presence of the added redox reactant. Two limiting
cases are expected. The first one is observed when the rate of redox transformation within the polymer after addition of redox reactant is low compared to the rate of spontaneous processes in the absence of such reactant. In this case, the added redox reactant has a small interfering effect on the potential. In the second case (low rate of spontaneous processes in the absence of redox reactant), the interference from the redox species is strong.

To obtain the meaningful data, special precautions are necessary. The applied current should be small enough not to alter ion concentration close to the polymer surface, and the ohmic potential drop should be negligibly small. For the currents in the range of mA and electrolyte concentration higher than $10^{-5}$ mol L$^{-1}$, both conditions are fulfilled. To minimize the error of $i_b$ determination, the applied current should induce potential changes of similar magnitude as observed under open-circuit conditions. Moreover, the range of potential changes should be relatively narrow, justifying the assumption of constant $C$.

**RESULTS AND DISCUSSION**

**Potential transients**

As already discussed in the Theoretical section, potential transients of CP-coated electrodes upon contact with redox reactant are expected different, depending on the properties of the couple and the polymer film. An example of case 1 (high capacitance, high reaction rate) can be PPyCl film in the presence of $\text{Fe(CN)}_6^{3-}$ ions (Fig. 1). A PPyCl electrode was conditioned in 0.1 mol L$^{-1}$ KCl solution and then immersed into 0.1 mol L$^{-1}$ KCl solution containing 1 mmol L$^{-1}$ $\text{Fe(CN)}_6^{3-}$. A slow potential increase was recorded, suggesting that the rate of the process is controlled by reactant’s diffusion in the solution.

To support the above statement, theoretical potential values were calculated assuming fast charge transfer and diffusive transport as the rate-determining step. For this purpose, equation 3 was utilised assuming electrode surface area $A = 0.07$ cm$^2$, diffusion coefficient of $\text{Fe(CN)}_6^{3-}$ $D = 7.6 \times 10^{-6}$ cm$^2$ s$^{-1}$ (in solution) [38], and $c = 1$ mmol L$^{-1}$. Capacitance $C = 3$ mF was determined from the potential – independent part of the voltammetric curve of PPyCl of the same thickness (current/scan rate) recorded in 0.1 mol L$^{-1}$ KCl and corresponding to the oxidized state of the polymer. The resulting dependence is presented in Figure 1. It shows an excellent correlation of experimentally obtained and calculated $\Delta E_{OCF}$ values for $t < 50$ s, and thus confirms that diffusion of the reactant is the rate-determining step. For longer times, the recorded potential approaches the equilibrium redox potential value and Cottrell’s equation does not hold any more.
Interfering influence of redox reactants on potentiometric responses

An example of case 2 (high capacitance, low charge transfer rate) is oxidation of polypyrrole film by oxygen. The corresponding experimental results are presented in Figure 1 (t = 0 refers to the moment when deoxygenated KCl solution is in contact with air). Potential increase is considerably slower than in the above discussed case of Fe(CN)$_6^{3–}$ reduction — only a few mV change within this time range, which points at some limitations in charge transfer rate.

An example of case 3 (low capacitance, high charge transfer rate) is reduction of Fe(CN)$_6^{3–}$ ions by polypyrrole doped with dodecylsulfate ions [27]. In this case, the potential instantaneously approaches the final stable value (results not shown).

The influence of other redox reactants: H$_2$O$_2$ ($E_0 = 1.55$ V vs Ag/AgCl), S$_2$O$_8^{2–}$ ($E_0 = 1.79$ V), and I$_2$ ($E_0 = 0.31$ V) having different redox potentials and charge transfer kinetics has been also investigated. Figure 2 illustrates time changes of the open-circuit potential for polypyrrole electrodes immersed in the solution: 0.1 mol L$^{-1}$ KCl + 1 mmol L$^{-1}$ oxidizing agent. The observed potential increase results from polypyrrole oxidation in the presence of redox reactant. In case of PPyCl, potential changes were small compared to theoretical changes expected for diffusion-controlled process. Theoretical values were calculated assuming 2-electron process and $D = 1 \times 10^{-5}$ cm$^2$ s$^{-1}$. In contrast to the influence of Fe(CN)$_6^{3–}$ (Fig. 1), a considerable difference between the calculated and experimental results has been observed. This discrepancy results from the low charge transfer rate between the redox reactant and the conducting polymer (similar results were recorded for PPyFeCN, data not shown).
Figure 2. The time change of the open-circuit potential for PPyCl films (polymerisation charge: \(2.8 \text{ C cm}^{-2}\)) in the presence of redox reactants (concentration: \(10^{-3} \text{ mol L}^{-1}\)). Thin line: theoretical plot calculated from equation 3, assuming linear diffusion as rate determining step.

For all reagents tested, the observed relation is similar to that recorded for oxygen; however, the effect of the studied redox species is slightly stronger (cf. Fig. 1). Their influence on ionic potentiometric characteristics of polypyrrole electrodes is presented in Figure 3A and B. For both PPyCl and PPyFeCN the characteristic shape of the potential vs logarithm of KCl concentration plot is still observed. However, in the presence of the redox reactant the plots are shifted to higher potentials and their slopes are decreased. The magnitude of the observed influence corresponds strictly to the sequence of charge transfer rates, deduced from Figure 2. The smallest influence was recorded for \(\text{H}_2\text{O}_2\) (the smallest changes in the potential, Figure 2), while the strongest for \(\text{S}_2\text{O}_8^{2-}\), being the strongest oxidant (the highest redox potentials, the highest rate of polymer oxidation, Figure 2).
Interfering influence of redox reactants on potentiometric responses

Influence of spontaneous processes of CP

As already discussed in the Theoretical section, the influence of the added redox interferents on stable potential of the polymer electrode depends on the rate of spontaneous charging/discharging processes. This rate can be different for various polymers and doping ions.

To study how the magnitude of redox interferences is related to charging/discharging processes, \( i_b \) current values were determined in the presence and absence of redox reactant (from equation 7), and compared. \( \text{Fe(CN)}_6^{3-} \) and \( \text{Fe(CN)}_4^{2-} \) served as

![Figure 3. Potentiometric characteristics recorded for PPyCl (A) and PPyFeCN (B) in KCl solutions in the absence (circles) and presence of 10\(^{-4}\) mol L\(^{-1}\) redox reactants: \( \text{H}_2\text{O}_2 \) (squares), \( \text{I}_2/\text{I}^- \) (triangles) and \( \text{S}_2\text{O}_8^{2-} \) (diamonds). Polymerization charge: 2.8 C cm\(^{-2}\).](image-url)
model examples. The measurements were carried out in $10^{-4}$ mol L$^{-1}$ KCl solutions (PPyFeCN, PMPyPSS, PEDOT-PSS) or $10^{-4}$ mol L$^{-1}$ NaClO$_4$ solution (PPyClO$_4$). Under conditions of galvanostatic polarization, potential depended linearly on time, confirming the assumption of constant $C$ within the studied potential range (exemplary data presented in Figure 4).

![Figure 4](image.png)

**Figure 4.** Potential vs time dependences obtained under conditions of polarized electrode potentiometry using either anodic or cathodic current in $1 \times 10^{-4}$ mol L$^{-1}$ NaClO$_4$ (PPyClO$_4$, applied current $1 \times 10^{-7}$ A) or $1 \times 10^{-4}$ mol L$^{-1}$ KCl (PPyFeCN, applied current $8 \times 10^{-8}$ A), in the presence of $1 \times 10^{-4}$ mol L$^{-1}$ Fe(CN)$_6^{4-}$.

The results obtained in $1 \times 10^{-4}$ mol L$^{-1}$ KCl (NaClO$_4$) solutions are collected in Table 1. The nature and the magnitude of the currents recorded in the absence of redox reactants were discussed elsewhere [37]. The negative value of the current recorded for anion-exchanging PPyClO$_4$ corresponds to the potential drift toward lower values, *i.e.* the process coupled with the anions’ release. On the other hand, for cation-exchanging PPyFeCN, PMPyPSS, and PEDOT-PSS the current is positive (potential increase) and the process is accompanied by the cations’ release. As already mentioned, in all these cases the release of ions from the polymer can be explained in terms of better availability of ions within the polymer, compared to dilute solutions. The current measured for PPyClO$_4$ is significantly higher than for other polymers.
Interfering influence of redox reactants on potentiometric responses

After addition of the redox reactant (either 0.1 mmol L\(^{-1}\) Fe(CN)\(_6^{3-}\) or Fe(CN)\(_6^{4-}\)) the results depend on the polymer used. In contrast to other polymers, for PPyClO\(_4^\cdot\) there exists only a slight influence of the added redox species on the recorded \(i_b\). This effect is due to considerably higher \(i_b\) current in the absence of the added redox reactant. The rate of Fe(CN)\(_6^{3-}\) reduction or Fe(CN)\(_6^{4-}\) oxidation is low compared to that of the spontaneous discharge process. Therefore, either Fe(CN)\(_6^{3-}\) or Fe(CN)\(_6^{4-}\) is expected to exert a weaker interfering influence on the potential of PPyClO\(_4^\cdot\) compared to other polymer film.

This conclusion was verified by recording ionic potentiometric characteristics in KCl solutions of different concentrations, in the absence and presence of redox interferent: a Fe(CN)\(_6^{3-4-}\) couple. The results are presented in Figure 5. In the absence of the redox couple, the slopes of the obtained dependences reflect ion-exchanging properties of the film (Tab. 2). In the presence of Fe(CN)\(_6^{3-4-}\) redox couple the absolute values of the slopes for the most of the studied films are considerably lower, except for PPyClO\(_4^\cdot\). Since the added redox reactant exerts a slight influence on \(i_b\) values of this film (Tab. 1), the slopes of the potentiometric dependences recorded in the presence and absence of the redox couple are similar. In contrast, but in agreement with the above considerations, PEDOT-PSS is characterized by the lowest \(i_b\) and thus the influence of the redox couple on the potentiometric dependence is the strongest. For PMPyPSS and PPyFeCN films, potential vs logarithm of KCl activity dependences are similar and much less pronounced compared to those of the redox couple – free sample. This is an intermediate case between PPyClO\(_4^\cdot\) and PEDOT-PSS. Due to the lack of linear proportionality between the potential and the logarithm of KCl activity in the presence of the redox couple, the measured potential differences for KCl concentrations of \(1 \times 10^{-1}\) mol L\(^{-1}\) and \(1 \times 10^{-5}\) are given in Table 2.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>(i_b) A</th>
<th>(10^2) mol L(^{-1}) KCl</th>
<th>(1 \times 10^2) mol L(^{-1}) KCl</th>
<th>(1 \times 10^5) mol L(^{-1}) KCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPyClO(_4^\cdot)</td>
<td>(-2 \times 10^{-7})</td>
<td>(-2.1 \times 10^{-7})</td>
<td>(-1.9 \times 10^{-7})</td>
<td></td>
</tr>
<tr>
<td>PPyFeCN</td>
<td>(2.5 \times 10^{-4})</td>
<td>(1.5 \times 10^{-8})</td>
<td>(3.5 \times 10^{-8})</td>
<td></td>
</tr>
<tr>
<td>PMPyPSS</td>
<td>(1.4 \times 10^{-4})</td>
<td>(5 \times 10^{-8})</td>
<td>(2.5 \times 10^{-8})</td>
<td></td>
</tr>
<tr>
<td>PEDOT-PSS</td>
<td>(7 \times 10^{-8})</td>
<td>(-0)</td>
<td>(2 \times 10^{-8})</td>
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</tr>
</tbody>
</table>

* For PPyClO\(_4^\cdot\) NaClO\(_4^\cdot\) was used instead of KCl.

Table 1. Mean values of currents corresponding to spontaneous charging or discharging of CP films in the absence and presence of the added redox reactants (Fe(CN)\(_6^{3-}\) or Fe(CN)\(_6^{4-}\)), calculated from equation 7.
Figure 5. Potentiometric characteristics recorded in KCl solutions in the absence (thick line) and presence of $1 \times 10^{-4}$ mol L$^{-1}$ Fe(CN)$_6^{3-/4-}$ couple (thin line).

Table 2. Parameters of potential vs logarithm of KCl activity dependences (Fig. 5) in the absence and presence of Fe(CN)$_6^{3-/4-}$ redox couple; concentrations of both redox forms: $10^{-4}$ mol L$^{-1}$

<table>
<thead>
<tr>
<th>Polymer film</th>
<th>Slope ± SD / mV dec$^{-1}$ (absence of redox couple)</th>
<th>Potential difference (mV) between KCl solutions: 0.1 and $1 \times 10^{-4}$ mol L$^{-1}$ (presence of redox couple)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPyClO$_4$</td>
<td>$-51.4 \pm 1.9$</td>
<td>$-156$</td>
</tr>
<tr>
<td>PPyFeCN</td>
<td>$43.3 \pm 2.3$</td>
<td>$120$</td>
</tr>
<tr>
<td>PMPyPSS</td>
<td>$56.2 \pm 0.5$</td>
<td>$66$</td>
</tr>
<tr>
<td>PEDOT-PSS</td>
<td>$57.1 \pm 0.2$</td>
<td>$36$</td>
</tr>
</tbody>
</table>

For the most stable (the lowest $i_p$) PEDOT-PSS polymer, ionic potentiometric dependence deteriorates for the redox couple concentration as low as $1 \times 10^{-5}$ mol L$^{-1}$ [39].

The above results show that the same redox reactant present at the same concentration has different interfering influence, depending on the kind of the polymer and the doping anion. Redox sensitivity of the polymer is related to the rate of the spontaneous charging/discharging. This brings us to the surprising conclusion that the best
resistibility towards redox interferences is observed for relatively unstable polymers (with the highest $i_b$).

**CONCLUSIONS**

The results concerning redox interferences in ionic potentiometry with CP-coated electrodes give some indications for analytical application of such electrodes. The influence of redox interferents relates to: (1) potential transients and (2) final potential values.

For the first case, the lower influence is expected for reactants characterized by slow charge transfer rate (redox potential is of lower significance), as well as for thick layers of polymers of fast ion exchange (high redox capacitance resulting in slow potential changes in the presence of interferents). The measurements should be carried out in the unstirred solution in order to lower the transport rate of the interferent.

In the second case, the smallest influence of redox interferents on final stable potential value is observed for the systems: polymer + doping ion, characterised by the high rate of spontaneous charging/discharging processes.

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**REFERENCES**


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