

Studies on Spontaneous Discharge of Oxidized Polypyrrole and Poly(N-methylpyrrole)*

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Spontaneous processes of charging/discharging of conducting polymers affect analytical characteristics of potentiometric sensors using conducting polymer films as ion sensitive membranes (detection limit, selectivity, sensitivity to redox interferences). These effects also contribute to undesirable loss of charge accumulated in the polymer phase used in charge storing devices. For polypyrrole and its derivatives the charging process is mainly related to oxidation by oxygen or other oxidants present in solution. On the other hand, the nature of the discharge process of oxidized polymer is still not quite clear. This work is oriented towards revealing the nature of the discharge reaction of polypyrrole and poly(N-methylpyrrole). The significance of spontaneous processes, especially for analytical characteristic of potentiometric sensors based on conducting polymers, is highlighted. Therefore, the effect of electrolyte concentration, solution acidity, influence of oxygen, conditioning time and medium was studied. The results of potentiometric and coulometric studies support the thesis that the discharge process is related to the polymer deprotonation; its rate is affected by pre-polarization of the electrode and conditioning of the polymer film.

Key words: polypyrrole, poly(N-methylpyrrole), spontaneous discharge, deprotonation

Conducting polymers (CP) are promising materials for practical applications due to their versatility. These polymers possess features usually specific for different groups of materials such as metals, plastics or ion-exchanging membranes. For instance, due to coupled ionic/electronic conductivity and possibility of reversible oxidation/reduction these polymers can be used as electrochemical sensors of ions or as biosensors [1,2]. An analyte ion/molecule can interact with the conducting polymer membrane in course of ion exchange or oxidation / reduction. Thus, the chemical signal evoked can be converted into electrical one and transferred *via* the polymer layer to the electronic recording instrumentation. From the analytical point of view, one of the most interesting conducting polymers is still polypyrrole, used as sensing membrane both in potentiometric and amperometric (voltammetric) sensors.

The CP state is affected not only by interaction with the analyte, it can be also altered due to spontaneous processes of polymer charging/discharging [3]. These processes can be attributed to *e.g.*: (i) protonation in acidic solutions [4–8]; (ii)

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deprotonation in neutral or alkaline media, coupled with breaking of double bond conjugation and thus conductivity decrease [5,9]; (iii) oxidation by oxygen present in air or solution [10–13]; (iv) irreversible oxidation by nucleophilic species present in solution, leading to polymer degradation [14–20]; (v) coupled cathodic discharge and overoxidation leading also to the polymer degradation [20]; (vi) other redox reactions with solution components, *e.g.* metal ions [21]; (vii) open circuit polymerization reactions of oligomer molecules entrapped in the polymer lattice [22].

Under conditions of external polarization and relatively short time scale of the experiment, these effects usually are of low significance due to high interfacial charge exchange rate accompanying polarization changes. The spontaneous processes can be thus regarded as low, undesirable residual signals.

However, if conducting polymer is used as a sensing membrane or signal transducer under potentiometric (open circuit) conditions, the spontaneous processes mentioned above are the main charge transfer processes present in the system. Therefore, they can be a crucially important factor affecting the analytical parameters of these sensors. Since the charging/discharging is accompanied by ion flow between the polymer phase and sample solution, as a consequence analytically useful linear relation between potential and logarithm of ion activity can be strongly affected. Unexpectedly, these processes were usually taken into consideration neither in theoretical description of potentiometric sensors nor in interpretation of experimental results. Only recently, the role of spontaneous charging/discharging processes: oxidation by oxygen and discharge of oxidized polypyrrole was discussed from the point of view of detection limit of potentiometric ion sensors [23,24] and susceptibility towards redox interferents [25].

It was shown that due to ion flow, accompanying the spontaneous charging/discharging process, the release of dopant ions from the film into the adjacent dilute solution layer results in increase of analyte concentration in the sample solution, near the polymer surface, *i.e.* where the potential is originating. These processes are responsible for increased value of low detection limit of potentiometric ion sensors [23]. This sample oriented dopant ion flow can be prevented or its direction can be even reversed by using galvanostatic polarization, which results in significantly lowered detection limit or so called super-Nernstian response, respectively [23,24]. On the other hand, the presence of spontaneous charging/discharging results in enhanced resistibility towards influence of redox interferents [25,26]. The spontaneous processes exert a kind of buffering effect on the potential and, hence, compensating, to some extent, the influence of redox interferents.

Although the process of spontaneous polypyrrole charging as oxidation by oxygen was described in detail in the literature [10–13], the nature and mechanism of discharge processes of oxidized CPs is still obscure. A more detailed description of these phenomena would be useful because they are undesirable for many, not only analytical aspects of conducting polymers applications, *e.g.* they are responsible for charge losses when the polymer is used as a charge storing device. The aim of this work is to study the discharge process, especially from the point of view of its significance for

conducting polymer based potentiometric sensors. Therefore, this paper is particularly oriented towards the influence of electrolyte concentration, solution acidity, thickness of the polymer layer, conditioning of the electrode on the spontaneous discharge process and its reversibility. These factors strongly affect the analytical usefulness of sensors in which the CP acts either as a sensing membrane or signal transducer placed between solvent polymeric membrane and substrate in all-solid-state ion-selective electrodes.

In case of polypyrrole the discharge process is commonly interpreted as deprotonation [9]; however, its nature is not so obvious for polypyrrole N-derivatives. Thus, the results recorded for polypyrrole will be compared with those obtained for polypyrrole derivative: poly(N-methylpyrrole) to highlight the role of N bonded H atom. Additionally, the role of ion exchanging properties of the polymer film will be investigated, by comparing the results for the polymer doped by ClO_4^- ions (anion exchanging layer) or poly(4-styrenesulphonate) ions (PSS – cation exchanging film).

EXPERIMENTAL

The electrochemical measurements, using potentiometry, coulometry, cyclic voltammetry and electrochemical impedance spectroscopy (EIS) were performed in a conventional electrochemical cell with a working glassy carbon disk electrode of diameter 3 mm (Detektor, Poland), as the substrate for polymeric coatings, a silver/silver chloride in KCl (1 M) gel reference electrode (Detektor, Poland) and a platinum counter electrode. Potentiostat/galvanostat CH Instruments (USA) model 660 was used in all measurements. EIS studies were carried out in the frequency range from 1 Hz to 100 kHz, with potential amplitude 10 mV.

The electrochemical quartz crystal microbalance (EQCM) apparatus used in the studies was based on electronic design described in [27] and was constructed in Institute of Physical Chemistry (Warsaw) [28]. AT-cut quartz crystals (Phelps Electronics, Goleta, USA) of 5 MHz nominal resonant frequency and 14 mm diameter were used as mass sensitive oscillators.

Polypyrrole (PPy) and poly(N-methylpyrrole) (PMPy) doped by ClO_4^- ions or their counterparts doped by poly(4-styrenesulphonate) (PSS^-) anions (PPy(PSS) and PMPy(PSS), respectively) were deposited potentiostatically at $E = 0.7$ V on glassy carbon electrodes. The electrodes were previously polished by Al_2O_3 0.3 μm . The polymerization charge within the range of $30 \div 180$ mC was used, corresponding to the thickness $\sim 1.8 \div 10$ μm [29], or 20 mC in case of electrodes used in EQCM measurements. The polymerization solution was 0.1 M pyrrole or N-methylpyrrole in aqueous 0.1 M solution of NaClO_4 or NaPSS . After polymerization the electrodes were rinsed with water, immersed into 1 M KCl solution and polarized under conditions of cyclic voltammetry (in the range $-0.8 \div 0.5$ V, scan rate 25 mV s^{-1}) for 5 minutes.

Distilled pyrrole and N-methylpyrrole were kept in a refrigerator and prior to use they were purified by passing through an alumina gel column. Millipore water was used throughout this work. Other chemicals (p.a.) were used as received. In some experiments oxygen was removed from solution by bubbling argon through it. All measurements were done at ambient temperature ($21^\circ\text{--}24^\circ\text{C}$).

RESULTS AND DISCUSSION

The presence of spontaneous processes of charging/discharging of conducting polymers can manifest itself in different ways, depending on experimental conditions, *e.g.* as the change of the polymer coated electrode potential, CP conductivity or shape of voltammetric curves depending on the film history (polarization, conditioning). These processes also result in potential transients after anodic or cathodic polarization.

Fig. 1 presents open circuit potential *vs.* time dependences recorded after 3 minutes polarization at oxidizing potential 0.5 V for PPy and PMPy. For these polymer layers, as well as for their PSS doped counterparts (data not presented), similar results were recorded. The potential slowly decreases reaching the value around 0.3 V (PPy) or 0.4 V (PMPy). The oxygen absence/presence does not affect the obtained dependences indicating that oxygen does not interact with the polymer in course of discharge process. The higher H^+ ions concentration in solution results in slower potential decrease in case of PPy, probably due to slower PPy deprotonation in acidified solution.

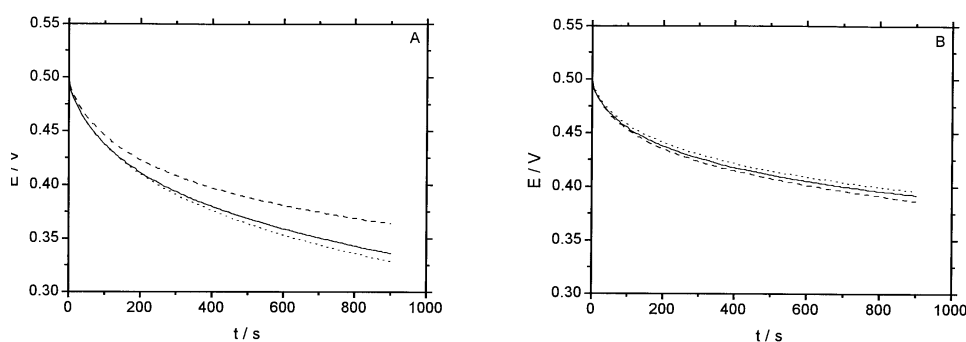


Figure 1. Open circuit potential *vs.* time dependences after 3 minutes polarization at oxidizing potential 0.5 V for PPy (A) and PMPy (B) layers in 1 M KCl (solid line), 1 M KCl + 0.01 M HCl (dashed line) and deaerated 1 M KCl (dotted line). Polymerization charge: 150 mC.

From the point of view of polymers applications in ion sensors, the influence of electrolyte ions concentration on the spontaneous discharge is especially important. One can expect that due to electroneutrality condition the discharge process should be coupled with release of anions or incorporation of cations, depending on the ion exchanging properties of the polymer. Therefore, electrolyte concentration should affect the shape of potential *vs.* time dependences and moreover, the results for PSS doped polymers are expected to be different from those obtained for layers doped by mobile anions.

The results presented in Fig. 2: the potential vs. time dependences for chosen electrolyte (KCl) concentrations confirm the difference of transients for PPy and PPy(PSS). In the former case, the potential – time relation is almost independent of electrolyte concentration, while for PPy(PSS) the rate of potential decrease is significantly higher for lower KCl concentrations.

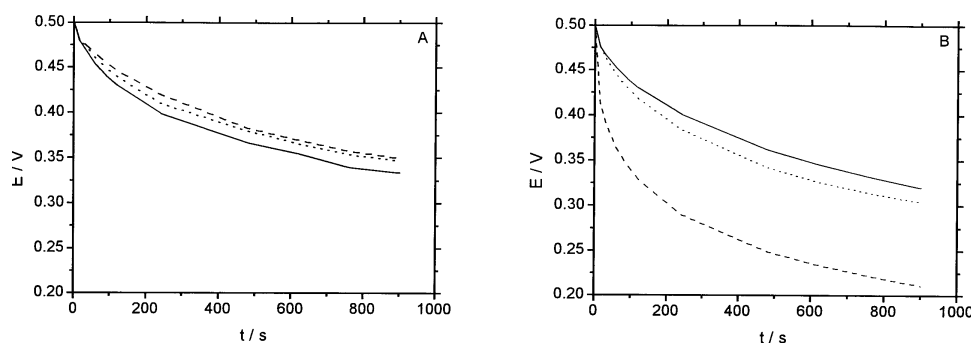


Figure 2. Open circuit potential vs. time dependences after 3 minutes polarization at 0.5 V for PPy (A) and PPy(PSS) (B) layers in KCl solutions of variable concentration: 1 M KCl (solid line), 0.1 M KCl (dotted line) and 0.01 M KCl (dashed line). Polymerization charge: 150 mC.

Explanation of this behaviour requires a deeper insight into the discharge process; potentiometric data itself is not sufficient to explain the difference. Using the procedure described in [3], the time dependences of charge flowing across the polymer/solution interface under open circuit conditions (as a result of spontaneous discharge) were determined. The electrode was initially polarized at 0.5 V for 3 minutes and the circuit was disconnected for a time period, t . In subsequent step the potential 0.5 V was applied again and the anodic charge was measured. This charge was assumed to be equal to that lost due to open circuit discharge.

Exemplary plots charge vs. time obtained for PPy and PMPy are presented in Fig. 3. Similar results were observed for PSS doped films (results not shown). The polymerization charge (film thickness) significantly affects the amount of flowing charge. As expected, for thicker films it is higher; nevertheless, in dilute KCl solutions the charge changes in time are much slower. Comparing the obtained charge, Q , in 1 M KCl with the total positive charge that can be stored in the layer, Q_{stored} (estimated from cyclic voltammetric curve recorded in the range from -0.8 V to 0.5 V), the discharge ratio, Q/Q_{stored} , can be evaluated for arbitrary chosen experiment time, 15 minutes of open circuit conditioning. This ratio is close to 0.1, regardless the film thickness.

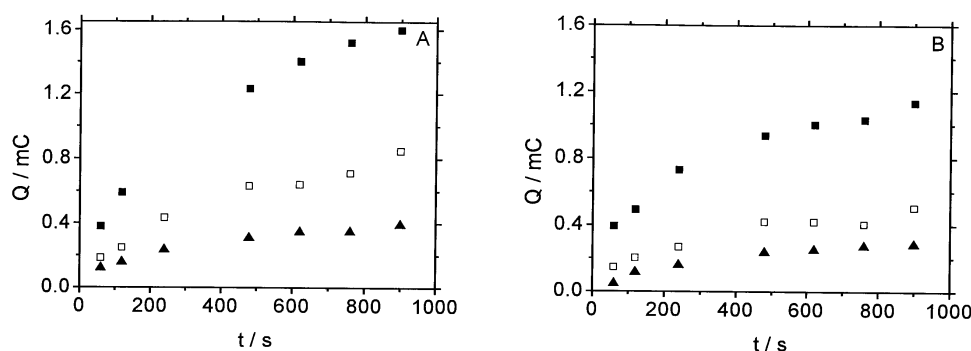


Figure 3. Charge vs. time dependences for PPy (A) and PMPy (B) layers. (■) – 1 M KCl, polymerization charge: 150 mC; (□) – 0.1 M KCl, polymerization charge: 150 mC; (▲) – 1 M KCl, polymerization charge: 30 mC.

Charge vs. time curve's shape suggests that the dependence is exponential:

$$Q = Q_0[1 - \exp(-kt)] \quad (1)$$

i.e. first-order reaction kinetics obeys, with rate constant, k , and Q_0 as maximal charge accumulated in the polymer film. By fitting the exponential curve, both k and Q_0 could be estimated. The k constant was found to be virtually independent of the polymer tested, its ion exchange properties, film thickness and electrolyte concentration, it was close to $4 \cdot 10^{-3} \text{ s}^{-1}$ in all cases. Only for PPy(PSS) this rate constant is slightly higher in 0.01 M KCl solution, approaching 10^{-2} s^{-1} . On the other hand, Q_0 was found to be considerably dependent on the film thickness and electrolyte concentration (Fig. 4). For 1 M KCl and all polymers studied the change of Q_0 is almost proportional to the polymerization charge. With decreasing concentration of the electrolyte the increase of Q_0 with the polymerization charge (film thickness) becomes smaller. This result indicates that charging/discharging process in the concentrated KCl solution occurs in the whole volume of the polymer layer, while for low concentration it is limited to the near surface layer of the polymer. This effect is most probably due to slow charge propagation in the polymer film, as indicated by a high ionic resistance of polypyrrole films in dilute electrolyte solutions [30,31]. It should be noted that the decrease of Q_0 accompanying lowering KCl concentration for PPy(PSS) is smaller than for PPy of the same polymerization charge.

It is interesting to compare the charge changes occurring in time under open circuit conditions with accompanying changes of the open circuit potential, obtained from a separate experiment. Fig. 5 shows a linear relation between Q and E , pointing to a constant value of low frequency capacitance value in the studied potential range, corresponding to the oxidized state of the polymer, both in concentrated and dilute solutions. The capacitance value obtained for 1 M KCl is consistent with that obtained from cyclic voltammetry experiment or EIS measurements for low frequencies; de-

noting that the capacitance of the polarized electrode is the same as under open circuit conditions. With lowering KCl concentration the capacitance significantly decreases, in 0.01 M solution it is almost 10 times lower than in 1 M KCl solution (Table 1). The dependence of the capacitance value on electrolyte concentration can result from the presence of pores in the polymer structure, filled with electrolyte solution [30,31]. Moreover, the determination of capacitance in dilute solution basing on voltammetric data is not straightforward due to influence of uncompensated solution resistance. Therefore, using the above described method, with no external polarization, capacitance values in dilute solutions can be obtained, unbiased by the resistance influence.

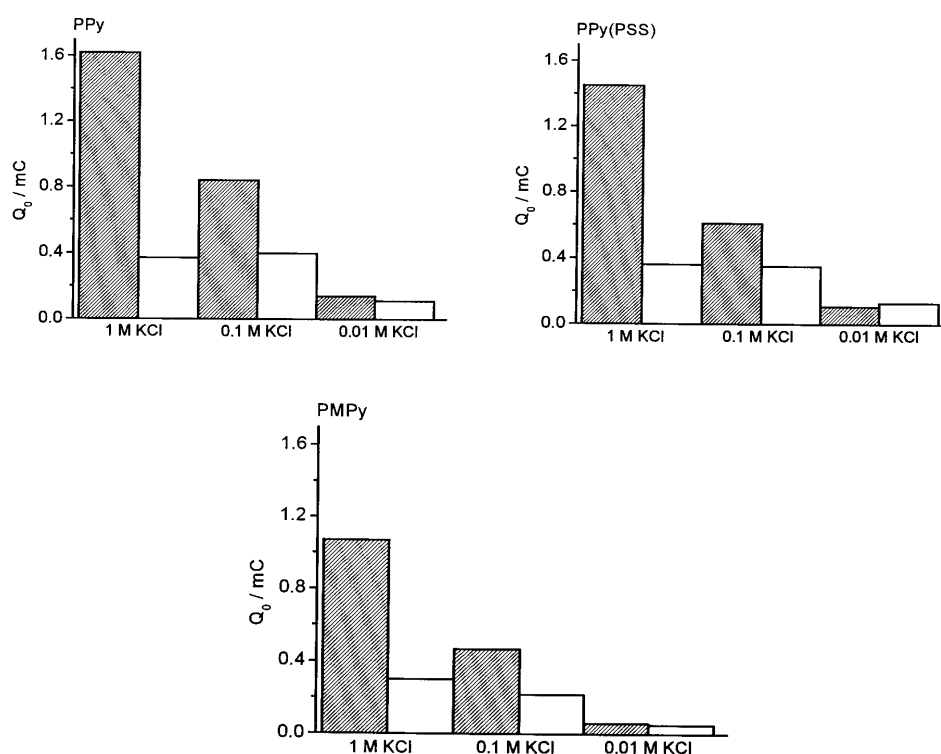


Figure 4. Maximal charges (Q_0) accumulated in polymer layers for different KCl concentrations. Polymerization charge: 150 mC (shaded area) and 30 mC (blank area).

The linear form of relation between the charge and the potential is of major practical significance, because, under open circuit conditions, the shape of E vs. time dependence is the same as that of charge vs. time, reflecting the kinetics of discharge process.

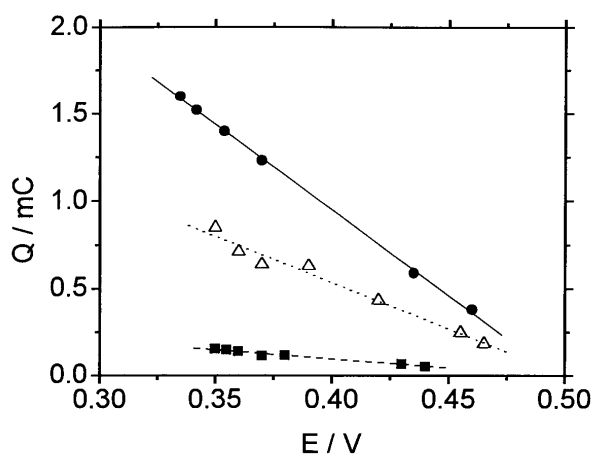


Figure 5. Charge related to spontaneous discharge vs. open circuit potential for PPy layer (polymerization charge: 150 mC), obtained from charge vs. time and potential vs. time dependences.

Electrolyte concentration: 1 M KCl (●, solid line), 0.1 M KCl (Δ, dotted line), 0.01 M KCl (■, dashed line); $Q = 0$ mC for $E = 0.5$ V.

Table 1. Capacitance values of PPy layers in solution of different KCl concentration. Polymerization charge: 150 mC.

KCl concentration/M	Capacitance/mF
1	9.8
0.1	5.3
0.01	1.1

Since the time dependence of the flowing charge points to first-order reaction, the rate of charge changes, Q , is simply expressed as:

$$\frac{dQ}{dt} = -k \cdot Q \quad (2)$$

Assuming the invariance of the capacitance, C , during the experiment, the above equation can be rewritten in the form:

$$\frac{dQ}{dt} = -k \cdot C \cdot E \quad (3)$$

Since the rate of charge change can be easily expressed by the change of potential:

$$\frac{dE}{dt} = \frac{1}{C} \cdot \frac{dQ}{dt} \quad (4)$$

joining equations 2–4, one can write:

$$\frac{dE}{dt} = -k \cdot E \quad (5)$$

Thus, the potential changes rate should be independent of the electrolyte concentration and ion-exchange properties of the conducting polymer layer. Fig. 2 presents the time dependence of potential after anodic polarization for PPy and PPy(PSS). According to above expectations, for PPy the potential decrease rate is virtually independent of KCl concentration; however, for PPy(PSS) the rate of potential decrease is higher in more dilute solutions. The observed non-symmetric influence of electrolyte concentration on the potential transients for PPy and PPy(PSS) can be explained by mentioned earlier increased rate constant value for the latter polymer in dilute KCl solution.

The next problem to be discussed is the nature of the discharge process because different processes can be responsible for the potential decrease of oxidized polymers and accompanied discharge. The following possibilities can be taken into consideration: (a) reduction of the polypyrrole film with simultaneous oxidation of water to molecular oxygen; (b) concentration gradient of oxidized forms of the polymer due to oxidation at positive potential – the concentration near the electrode surface is higher than in the polymer bulk, under open circuit conditions this concentration gradient disappears due to relaxation, thus a potential drift is observed; (c) irreversible oxidation of the polymer accompanied by its reversible reduction connected with release of dopant ions [20]; (d) reduction of the polymer coupled with simultaneous oxidative polymerization of oligomers entrapped in the polymer matrix [22] (oxidation potentials of oligomers is lower than that of monomer molecule), in case of anion exchanging polymer this process is connected with release of protons and counter ions; (e) deprotonation of the polymer, similarly as in the case (d) the process is coupled with release of protons and counter ions.

The formal potential of the O_2/H_2O couple in neutral solutions is close to 0.6 V vs. silver/silver chloride electrode. This potential is higher than that recorded during spontaneous discharge. Therefore, the water oxidation process (a) cannot be responsible for the spontaneous discharge of polypyrrole or poly(N-methylpyrrole).

In case of concentration polarization (case (b)), the relaxation time can be estimated from the relation: L^2/D , where L is the film thickness, while D is diffusion coefficient. Taking into account typical values: $D = 10^{-9} \text{ cm}^2 \cdot \text{s}$ and L around $2 \mu\text{m}$ (polymerization charge: 30 mC), the estimated relaxation time is close to 40 s, *i.e.* much lower than observed experimentally.

The most probable reason of polymer discharge is deprotonation (process (e)) [4,5]. Deprotonation is a kind of polymer dedoping and can be accompanied by potential change. As shown recently [32], acidification/alkalization of solution results in increase/decrease of the open circuit potential of polypyrrole electrode.

However, cases (c) and (d) cannot be excluded as a reason of the discharge. The difference between these cases lies in reversibility of processes involved. Deprotonation (e) is reversible, in contrary, the polymerization of oligomers (d) or profound oxidation of the polymer are irreversible reactions (c).

The further studies concerned the influence of prolonged anodic polarization on the discharge effect. Fig. 6 presents the influence of 0.5 V polarization time on the open circuit potential vs. time dependences. Extended polarization time within the range from 180 s to 2 hours, corresponds to slower potential changes under open circuit conditions, directly after disconnection of the electrochemical cell, *i.e.* the potential is more stable. For longer polarization times, exceeding 2 hours, only slight improvement of potential stability is observed. The observed response can be an effect of the following reasons: completion of slow deprotonation process at 0.5 V (*i.e.* case (e)), polymerization of oligomers or irreversible oxidation is complete at this potential (case (d) and (c)) or mobility of doping anions in the film becomes lower while the electrode is polarized, thus anions release accompanying the discharge process is slower. The latter effect can result from some structure rearrangement of the polymer in the electric field.

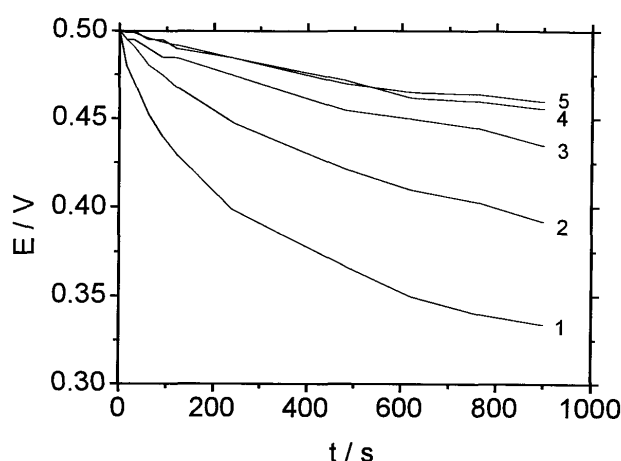


Figure 6. Open circuit potential vs. time dependences for PPy layer in 1 M KCl just after polarization at 0.5 V carried out for: 180 s (line 1), 30 minutes (line 2), 2 h (line 3), 6 h (line 4), 12 h (line 5).

The following experimental procedure was proposed to distinguish cases (c), (d) and (e). Polypyrrole films were polymerized as above and the potential-time dependence was recorded after 3 min polarization at 0.5 V. In a parallel experiment the polymer films were alternately polymerized at 0.7 V for 2.5 minutes and polarized at 0.5 V for 27.5 minutes. The latter polarization was aimed to complete polymerization of oligomers (avoiding polymerization of monomer molecules) or irreversible oxidation corresponding to potential 0.5 V. However, the potential vs. time dependence recorded after above described preparation of films was very similar (within limits of experimental error) to that obtained using the typical polymerization procedure, with

no polarization at 0.5 V. This result confirms that neither polymerization of oligomers nor possible irreversible oxidation is the crucial factor responsible for the polymer discharge.

As stated above, it is rational to assume that in case of deprotonation as the mechanism contributing to observed CP discharge, the effect of long polarization will be reversible. To study this effect diverse conditioning procedures were applied, following polarization at 0.5 V for 2 hours. Then, the electrode was polarized again at 0.5 V (for 3 minutes) and immediately the open circuit potential vs. time dependence was recorded. The results obtained for PPy and PMPy are collected in Fig. 7 and compared to the result of experiment (curve 1) with only usual 3 minutes polarization. As described above, the rate of potential decrease after 2 hours polarization is much lower than for the process represented by curve 1. However, after 2 hours polarization and subsequent 2 hours open circuit conditioning in KCl solution the rate of potential decrease is slightly higher (curve 5), especially after conditioning in acidified solution (curve 4) or polarization at 0 V, promoting film protonation (curve 3). The effect of conditioning time on the shape of potential vs. time dependence is even more pronounced for longer conditioning times (8 hours in 1 M KCl, curve 2). These results show that the initial shape of potential vs. time dependence can be regained, *i.e.* the effect of its change is reversible. Moreover, this initial state can be faster regained after conditioning in acidic solutions showing that reversible deprotonation is mostly responsible for observed polypyrrole or poly(N-methylpyrrole) discharge.

All these results suggest that slow polymer discharge observed after long anodic polarization is a consequence of decreased counter ions mobility in the film. This behaviour can be revealed by EIS results. Fig. 8 presents complex plane impedance plots for PPy polarized at 0.5 V for 3 minutes and 2 hours. In both cases typical spectra

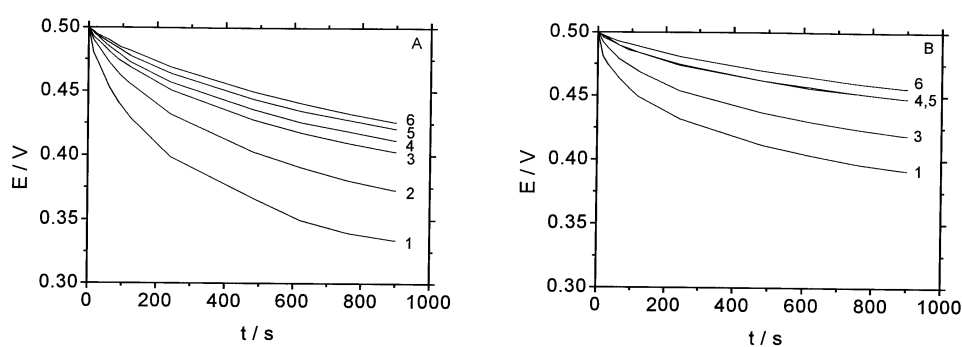


Figure 7. Open circuit potential vs. time dependences for PPy (A) and PMPy (B) layers (polymerization charge: 150 mC): 1 – 3 minutes polarization at 0.5 V in 1 M KCl; 2 – 8 hours conditioning in 1 M KCl; 3 – 2 hours polarization in 1 M KCl at 0 V; 4 – 2 hours conditioning in 1 M KCl + 0.01 M HCl solution; 5 – 2 hours conditioning in 1 M KCl; 6 – 2 hours polarization at 0.5 V in 1 M KCl.

were obtained, with almost vertical line pointing to purely capacitive behaviour at low frequencies and Warburg region for higher frequencies. After long polarization a significant extension of the Warburg region can be noticed, pointing to lower ionic mobility [33] in this case. Applying the transmission line model for porous oxidized polymer, the ionic resistance of polypyrrole layer, R_I , can be determined from equation [33]:

$$R_I = 3(Z'_{\text{low}} - Z'_{\text{high}}) \quad (6)$$

where Z'_{low} and Z'_{high} are resistances corresponding to the low and high frequency end of the Warburg range, respectively. The ratio of R_I values obtained after 2 hours and 3 minutes polarization is around 2.4. A higher ionic resistance denoting lower counter ion mobility implies slower deprotonation accompanying anions release. The calculated ratio of ionic resistances is comparable with the ratio of open circuit potential decrease rates after the above mentioned polarization times (Fig. 6). As a consequence, longer time is needed to complete the discharge process (long conditioning in KCl solution is necessary to recover a fast potentiometric transient). On the other hand, conditioning in acidic solution or cathodic polarization is connected with incorporation of additional loosely-bound protons and counter ions. These ions can be easily released under open circuit conditions in neutral KCl solution.

The above described studies were supplemented by results of EQCM measurements. For PPy a slow frequency increase was observed after anodic polarization, resulting from release of dopant anions accompanying deprotonation [24]. Fig. 9 presents potential and frequency vs. time relation, recorded under open circuit condi-

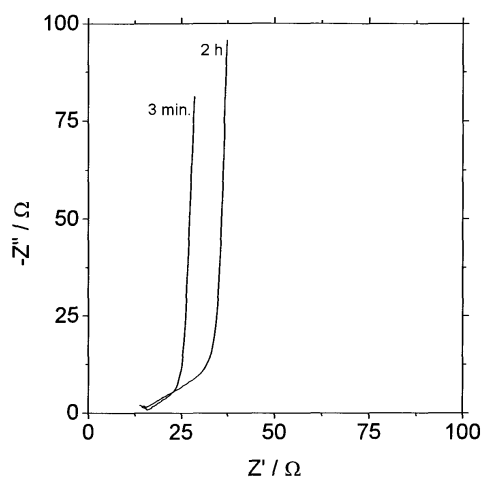


Figure 8. EIS spectra of PPy (polymerization charge: 30 mC) in 1 M KCl solution after polarization time at 0.5 V: 3 minutes and 2 hours.

tions for PPy(PSS) just after polarization at 0.5 V in KCl and HCl solutions. In KCl solution the potential decrease is accompanied by frequency decrease, pointing to mass increase resulting from exchange of H^+ with solution K^+ cations. The experiment carried out in HCl solution ("replacement" of H^+ ions from the polymer with H^+ ions from the solution) demonstrates virtually no frequency (mass) changes. The open circuit potential is also virtually constant in time. Thus, spontaneous deprotonation is responsible for open circuit discharge of polypyrrole layers.

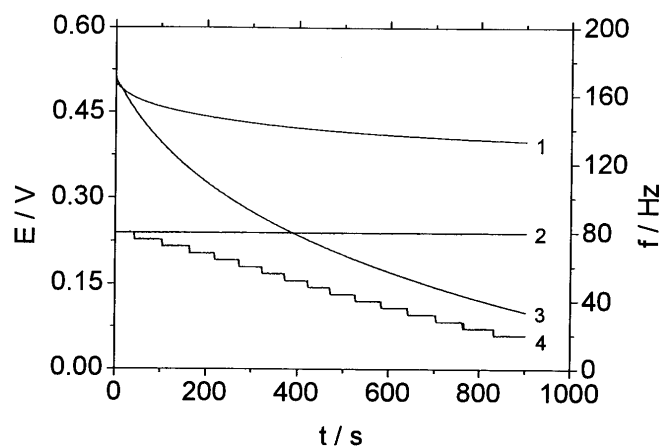


Figure 9. Frequency (f) (curves 2,4) or potential (E) (curves 1,3) vs. time dependences for PPy(PSS) layer in 1 M KCl (curves 3,4) and 1 M HCl (curves 1,2) after 2 h polarization at 0.5 V. Polymerization charge: 20 mC.

The results presented in this work helped us to answer the question of the discharge origin. Both our experimental results and literature data (*e.g.* [4,5,8,9] point to the deprotonation as the most important reason of the discharge under moderate conditions (not high anodic potentials applied during pre-polarization, relatively short experiment time) and thus important for analytical applications of conducting polymers. In the case of polypyrrole, protons might be released from the N–H bond in pyrrole ring. However, similar potential vs. time transient obtained for PPy and PMPy suggest another mechanism. Since in case of PMPy hydrogen atoms are not directly bound to nitrogen atoms, the release process can concern exchangeable H^+ ions, loosely bound to the polymer chain, playing the role of "protonic dopant" [8]. The additionally bound, doping H^+ ions can be collected in the polymer layer *e.g.* during polymerization. Similar process can occur also in the case of PPy because deprotonation connected with N–H dissociation seems not probable in neutral or acidic media used in our experiment. It occurs to considerable extent only in alkaline solutions, for $pH > 9$ [5].

These results suggest a simple manner to control the rate of spontaneous discharge, by pre-polarization of the electrode or a proper conditioning medium. Depending on requirements, *e.g.* in conducting polymer based potentiometric sensors, the discharge process can be exposed or suppressed.

CONCLUSIONS

Spontaneous processes of polypyrrole or poly(N-methylpyrrole) discharge are represented by release of protons doping the polymer, weakly bound to the polymer chain. These processes are of crucial importance for analytical applications of conducting polymers in potentiometric ion sensors because they affect their analytical characteristic (*e.g.* detection limit, selectivity, sensitivity to interferents).

The rate of spontaneous discharge is practically insensitive to the presence of oxygen; however, it is dependent on the presence of H^+ ions, electrolyte concentration and film thickness. It can be controlled by both polarization and conditioning mode. The discharge rate can be significantly suppressed by prolonged anodic polarization, while the initial rate can be regained by long conditioning, facilitated in the presence of acid in solution or by cathodic polarization.

Acknowledgments

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