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On the break-in and passivation phenomena in polypyrrole/sulfate films

Allan Hallik · Ants Alumaa · Jüri Tamm

Abstract The influence of different divalent cations (M^{2+}) on the electrochemical charging/discharging process of polypyrrole/sulfate (PPy/SO_4) films has been investigated. In principle, two different types of M^{2+} were found: (a) cations that cause the break-in phenomenon in the PPy film during electrochemical cycling with a gradual increase of film electroactivity and (b) cations in whose solutions the PPy film remains mainly electroinactive. Certain correlations have been drawn between several physico-chemical properties of the investigated cations and the break-in and passivation phenomena. The break-in and passivation phenomena were found to be influenced by the size and deformability of the cation hydration shell, ion covalent index and softness, as well as by the pH value of the test solution.

Keywords Polypyrrole · Sulfate · Divalent cations · Break-in · Passivation · Cycling voltammetry

Introduction

Due to the promising properties of conducting polymers, the redox processes occurring in these polymers (including PPy) have been widely studied. These studies have revealed that the total electrochemical process involves both anionic and cationic doping. In addition the quota of either component depends on many factors, among them the ion mobilities. Though a number of relationships have been found in previous studies, a number of questions have remained unclear concerning the electrical and mechanical changes in the PPy matrix during electrochemical cycling as well as the role of various ion properties in the redox behavior of conducting polymers.

The electrochemical measurements of many PPy/dopant films revealed the peculiarity of the first cyclic potential sweep as compared with the following sweeps. A continuous altering of its structure and increase of the film electroactivity were established in some cases during the redox cycling of the film. Moreover, the so-called break-in phenomenon may continue during a large number of cycles [1–7]. In the case of PPy/SO_4 layers in the solutions of monovalent cations (M^+), the first voltammogram differs from the following cycles, which in their turn are quite similar to one another [4, 8]. However, the break-in phenomenon, or its opposite, which is the electrochemical inactivation of the film, was established in the solutions of some M^{2+} [4]. These latter phenomena were ascertained by using some solutions of M^{2+} besides PPy/SO_4 films as well, as in the case of p-toluenesulfonate-doped PPy (PPy/Tos) and chloride-doped PPy (PPy/Cl) films [9, 10]. In references [10–12], it was found that the reduction process of the PPy/NO_3 film, as well as of the PPy/Cl film (both freshly prepared and conditioned/aged films) is strongly affected by double-charged cations present in the test solution. The effect of double-charged cations (as compared with the influence of monocharged cations) emerges in lowering of the reduction charge, changing of the shape of the CV curve, and also in the disappearance of the second (more negative) reduction peak.

Unlike the above-mentioned cases where M^{2+} ions in the test solution hinder the proceeding of redox processes in the film (partly or completely), in the case of PPy layers doped with big monovalent sulfate anions like dodecylsulfate

A. Hallik (✉) · A. Alumaa · J. Tamm
Institute of Chemistry, University of Tartu,
Jakobi 2,
51014 Tartu, Estonia
e-mail: allan.hallik@ut.ee

(DDS⁻), the presence of double-charged cations in the measuring solution can (as compared with the case of M^+), on the contrary, facilitate the proceeding of redox reactions [6]. Thus, the break-in or inactivation phenomena observed for different systems are not related solely to the presence of multivalent cations in the test solution, but to a suitable coexistence of the features of both the polymeric film and the solution. Here, such factors as the nature of the original dopant ion (univalent or bivalent; small, medium-sized or large) and also the charge, size, and hydration degree (or hydration enthalpy) of solution ions are of great importance [3, 4, 6, 9–17].

In references [4, 10, 11, 18, 19], the influence of the pH of the solution on the above-named phenomena was also established. The influence of pH may be twofold—in most cases, its decrease facilitates the redox process of PPy films, but in case of the PPy/Tos film [18] electrochemical inactivation was observed. A temporary increase of electroactivity was also found in case of the PPy/NO₃ film by transferring the film from a neutral to an alkaline solution [11].

According to the results presented in [6, 10], the electrochemically controlled transport of ions in PPy films improved with a decrease of Pauling's radius of the metal cation present in the test solution. This conclusion was found to be valid both for the PPy/well mobile dopant film (PPy/Cl) and the PPy/poorly mobile dopant film (PPy/DDS), although only for the first reduction scan in the latter case. For several PPy films doped with anions of low or very low mobility (mainly the anions containing sulfate and sulfonate groups, but also some other anions), the correlation between the improved flux ability of metal cations in the PPy matrix and the smaller hydrated radius (r_{hydr}) of these cations was established [6, 8, 15, 20, 21]. Yet, despite the existence of the above-mentioned tendencies for certain PPy/dopant/electrolyte systems, some discrepancies exist between "correct" and experimental dependencies [6, 15, 16, 20].

In addition to this, other principal deviations from the correlations discussed above were established. They include a lack of relationship (particularly) between transition metal ion mobility and its r_{hydr}, or in the case of some PPy/organic sulfate and PPy/organic sulfonate films the inability of certain M^{2+} to permeate polymer layers altogether [16, 17]. The peculiarity of the PPy/SO₄ film emerges from the tests performed in the solutions of various M^{2+} (but with close r_{hydr}), appearing in an essentially different redox behavior of the film [4]. The above-mentioned problems have remained definitively unsolvable even if some other PPy membrane structure and electrolyte parameters such as film isotropy, porosity, or stability constants for the dopant anion (A)—M^{n+} system have been taken into account. Therefore, with an aim to find out the factors determining the (different) response of PPy electrodes, an electrochem-

ical characterization was made of the redox behavior of the PPy/SO₄ films (as a sample for different effects). The investigated variables of the solution were different M^{2+} and pH.

Experimental

Polypyrrole films of about 3 μm thickness were synthesized galvanostatically on Pt-wire (0.1 cm²) electrodes at a current density of $i=2$ mA cm⁻² from aqueous solutions of 0.1 M pyrrole+0.1 M K₂SO₄ and (as reference films) 0.1 M pyrrole + 0.1 M NaCl. A Pt-wire was used as the counter electrode, and an aqueous saturated KCl|Ag|AgCl (Ag/AgCl) electrode was the reference electrode for synthesis and all CV experiments. Film thickness was calculated according to the relation 0.4 C cm⁻² per 1 μm [4]. Electrochemical measurements were performed in 0.1 M sulfate aqueous solutions saturated with Ar, containing metal cations of different size, charge, and nature (s and d metals): K^+, Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}. The pH values of the solutions were of two kinds: (1) as the concrete electrolyte originated, so the pH was 5.9(K^+), 4.8(Mg^{2+}), 3.3(Mn^{2+}), 3.7(Co^{2+}), 5.4(Ni^{2+}), 5.1(Zn^{2+}), 4.8(Cd^{2+}) and (2) adjusted to a fixed value (2.5, 3.0, 4.0, 5.0, 6.0) by using the solutions of H₂SO₄ or Ba(OH)₂. For comparison, the CV measurements were performed with PPy/SO₄ films in 0.1 M chloride solutions of different M^{n+}. The CV experiments were carried out within a potential interval from 0.4 V→ −0.8 V→0.4 V (Ag/AgCl) in a continuous cycling regime of 25 cycles, after which the CV data were saved; and in case of need, the next 25 cycles were taken. In one case, (Cd^{2+} ions) the lower limit of electrode potential was –0.7 V due to possible deposition of metal. The electrochemical measurements were performed using Autolab PGSTAT 30. Pyrrole (Aldrich) was distilled under a vacuum and kept refrigerated in the dark. The reagents of analytical grade were used as received. The solutions were prepared using Milli Q+ water. The test solutions were saturated with Ar (99.999).

Results and discussion

The influence of cations and anions on break-in and passivation phenomena

The cyclic voltammograms, representing two different behaviors of the same PPy/SO₄ film taken in the solutions of different M^{2+} are shown in Fig. 1. It becomes obvious that after repeated cycling, the "evolution" of the CV curve and redox charge takes place in the presence of Mn^{2+} ions in the solution (cf. curves 1 and 2), whereas in the case of
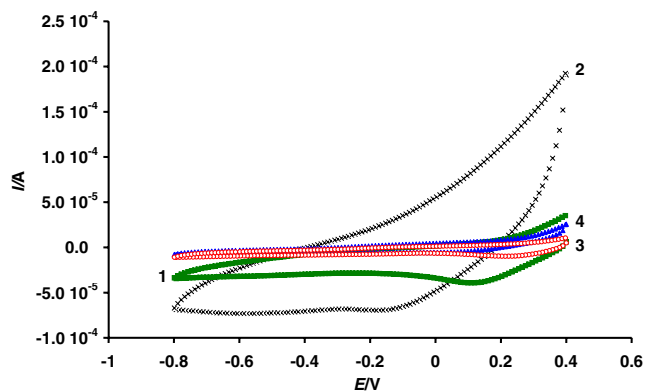
Fig. 1 Cyclic voltammograms of 3 μm PPy/SO$_4$ films in 0.1 M MnSO$_4$ (curves *1*, *2*) and NiSO$_4$ (curves *3*, *4*) solutions. First cycles (curves *1*, *3*) and 25th cycles (curves *2*, *4*). Scan rate 50 mV/s

Ni^{2+} ions the initial voltammogram remains practically unchanged (cf. curves 3 and 4). Similar differences in PPy/SO$_4$ film behavior in the solutions of different cations are observable in Fig. 2, presented as the dependencies of cathodic and anodic charges of the film on the CV cycle number. The curves in Fig. 2 show the belonging of Mn^{2+}, Mg^{2+}, and Co^{2+} ions to a group of ions enabling the break-in process during repeated scans of the PPy/SO$_4$ film. On the contrary, Zn^{2+}, Ni^{2+}, and Cd^{2+} ions in the electrolyte solution cause/retain the passivation of the PPy/SO$_4$ film. The quantitative data of reduction or oxidation charges obtained after 25 cycles and expressed as a percentage from the maximally possible charge obtainable with monovalent cations (K$^+$) are presented in Tables 1 and 2. It should be mentioned that the Q-cycle number curves, received in the solution of K$_2$SO$_4$ were parallel to *x*-axis, thus the red/ox charges were independent of cycle number. The calculated percentages in Tables 1 and 2 show that after 25 cycles, maximally one-third of the film electrochemically "works" (Mn^{2+}, Mg^{2+}); in the case of Co^{2+}, this part does not exceed one-fifth. The corresponding values for cations causing film passivation in the sulfate solution remain between 2.5% and 5%. From Fig. 2, it also becomes
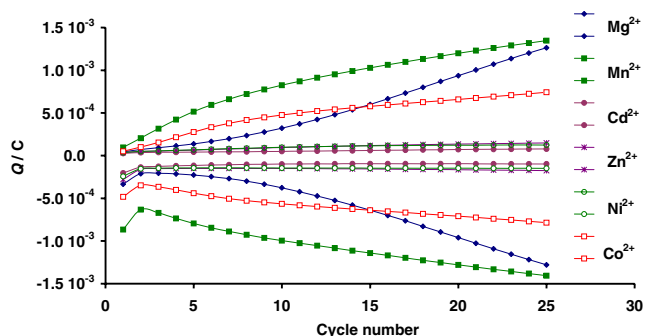
Table 1 The ratio of cathodic charges (%) of PPy/SO$_4$ films after 25 electrochemical cycles in 0.1 M sulfate solutions with M^{2+} and K$^+$, respectively

M^{2+}	Mn^{2+}	Mg^{2+}	Co^{2+}	Zn^{2+}	Ni^{2+}	Cd^{2+}
$Q(M^{2+})/Q(K^+)$	37.4	34.1	20.9	4.7	4.0	2.6

evident that the rate of the increase of the red/ox charge with each subsequent cycle (the slope of the curve) depends on the nature of the cation. This conclusion is valid for both types of the above-mentioned cations, although in the case of cations causing the passivation of the film, the slope and the total achievable charge is quite small. The data in Tables 1 and 2 also reveal the essentiality of the used electrolyte anion. Thus, while in the case of Mg^{2+} ions the $Q(M^{2+})/Q(K^+)$ is practically independent of the used electrolyte anion, in the solution of Mn^{2+} ions the presence of Cl$^-$ ions essentially hinders the break-in process. This feature is probably related to a partial redoping of the original PPy/SO$_4$ film by Cl$^-$ ions and the formation of a new film of mixed composition, PPy/SO$_4$/Cl, the behavior (as compared with the original film) of which is influenced by different M^{2+} ions diversely. Probably due to their large size and hydrophobicity, the tetrabutylammonium (TBA$^+$) ions, though being monovalent cations, belong to the group of passivating cations (Tables 1 and 2).

Collation of the obtained experimental data with various physico-chemical parameters of the investigated cations points out that the ability of ions to cause break-in or passivation phenomena is not attributable only to some of their single properties. This last conclusion is found to be valid, for instance, by trying to draw correlations between the revealed phenomena on one hand, and Pauling's crystallographic radii of M^{2+} or hydrated radii (r_{hydr}) of M^{2+}, also ionic mobilities, ionic potentials or ionic indexes of bivalent cations [22–24] on the other. It must also be stated that basing only on the porosity parameters of the PPy/SO$_4$ film (with its average pore radius of 18.5 Å, and having more than 50% of void volume [25]) and taking also into account the essentially smaller dimensions of (cat)ions, there should not be any essential difficulties in ion diffusion/migration in the film. Therefore, the existence of rather large mesopores in the PPy/SO$_4$ matrix cannot alone guarantee good accessibility of many (redox)active sites to moving (cat)ions, and likely the ions moving into the PPy/SO$_4$ matrix themselves have to create a certain kind of

Fig. 2 Dependence of cathodic and anodic charges on CV cycle number for PPy/SO$_4$ films (3 μm) in different 0.1 M sulfate solutions with cation, noted in figure

Table 2 The ratio of cathodic charges (%) of PPy/SO$_4$ films after 25 electrochemical cycles in 0.1 M chloride solutions with cation M^{n+} and K$^+$, respectively

M^{n+}	Mn^{2+}	Mg^{2+}	Sr^{2+}	La^{3+}	Ni^{2+}	TBA$^+$
$Q(M^{n+})/Q(K^+)$	8.3	33.2	6.0	6.6	6.8	2.5

microporosity in order to access these redox-active sites. Strong hindrances encountered by moving (cat)ions during the break-in/passivation process have found their expression in very low effective diffusion coefficient values (PPy/SO_4 films in the solution of $ZnSO_4$) [14]. The transport of the studied different M^{2+} to these sites is hindered to a various degree. According to our results, this depends on the pH of the solution (see "The influence of pH on break-in and passivation phenomena" section.) and on the size and deformability of the cation hydration shell. Ion transport is also affected by the ion covalent index and softness value [22–24, 26, 27], and by the selectivity properties of PPy pores (see "The selection of cations by differences in the charge, size and deformability of their hydration shell, also by their covalent index and softness values for different types" section.).

The influence of pH on break-in and passivation phenomena

It is well known that the pH values of different salt solutions (including sulfate solutions) are different owing to various reasons such as hydrolysis, different additions, etc. As already stated, the pH value of the solution has an influence on the phenomena studied in this paper. To make a difference between the influence of ion properties and the pH of a solution on break-in and passivation phenomena and to exclude the influence of random pH of the used electrolyte solution on the behavior of the PPy/SO_4 film, the electrochemical cycling of the films was additionally performed in the same sulfate solutions, but adjusted (as described in the experimental part) to a fixed pH value (2.5, 3.0, 4.0, 5.0, and 6.0). The obtained dependencies of cathodic and anodic charges of PPy/SO_4 films on the CV cycle number in certain representative sulfate solutions (Mg^{2+}, Mn^{2+}, Zn^{2+}) with different pH are given in Fig. 3. The comparison of plots (a–e) in Fig. 3, acquired at different pH values, demonstrated that the differences in PPy/SO_4 film behavior in the solutions of different M^{2+} ions became clearly evident only at pH≥4.0. At pH=3.0, and particularly at pH=2.5 the dependencies of cathodic and anodic charges on the CV cycle number coincided rather closely. This result pertains thereat to both gradually activating and passivating types of cations. For both activation causing cations—Mg^{2+} and Mn^{2+}, fairly similar behavior was achieved even at pH=4.0—see Fig. 3c. At higher pH values (pH=5 and pH=6), the differences are greater, especially at pH=5.0. Thus, while the ratio of cathodic charges $Q(Mg^{2+})/Q(Mn^{2+})$ between cycles 25–50 at pH=6.0 is constantly around 1.5, then surprisingly at pH=5.0 this ratio reaches corresponding values of two or more times higher, also showing growth as the number of cycles increases—see Fig. 3a,b. Peculiar to curves, representing the influence of Mg^{2+} cations, is an increase of their slope. This increase of slope begins after some preliminary cycles and the quantity of slope can significantly exceed the one obtained in the case of Mn^{2+} cations. This indicates that Mg^{2+} ions moving in and out of the film can, in a more effective way, change the structure of the PPy/SO_4 film in order to become better penetrable to ions in the following cycles.

Cathodic and anodic charges of the PPy/SO_4 film in the solution of a passivating cation (Zn^{2+}) at pH=5 or 6, change with 50 cycles only to a small extent—1.1-1.2 times and remain approximately 11-16 times lower than the corresponding values for Mg^{2+}. The charge increase approximately doubled in the present case when the pH of the solution was decreased to 4.0—see Fig. 3a,b,c. For one thing, the following decrease of the pH (pH<4) increases the importance of the influence of H^+ ions as complementary monovalent cations in the system, causing partial protonation of sulfate ions and suppression of the hydrolysis of M^{2+} ions.

The similarity of the shape of Q-cycle number curves, the obtaining of quite close Q values and the disappearance of differences in behavior between breaking-in and passivating cations in more acidic (pH=3.0) solutions as well as the continuing strengthening of these effects at pH=2.5, indicates that the redox process of the PPy/SO_4 film in acidic solutions does not proceed further under the domination of the features of different M^{2+} but is strongly affected by changes in the PPy structure caused and made uniform and poorly changeable by the influence of H^+ ions. As suggested by Zhang et al. [28] an essential decrease of the pH of the solution will lead to the protonation of nitrogen atoms or the selective adsorption of H^+ ions on the surfaces of PPy. Because of this, PPy can possibly undergo molecular structure changes or rearrangements at the polypyrrole/water interface, which affect the electric properties of PPy in aqueous solutions. The established more complete dedoping of PPy/SO_4 film after electrochemical reduction in more acidic solution [4] and the increasing of measured ionic diffusion coefficients with increasing of H^+ ions concentration in test solution [19, 29] also point to the favored structural changes (observing ion mobility) at a lowered pH. The effect of the cation (H^+ among this) was found to be higher on the occasion of anions of lower mobility [29]. Despite a certain facilitating influence of H^+ ions on cation mobility in the PPy/SO_4 film in the solutions of a lower pH (especially on passivating cation mobility), the total charge gain still remains essentially below the feasible gain, realized by using monovalent (K^+) cations. Thus these charges, being somewhat higher at pH=2.5 than at pH=3.0, generally remain between a half (pH=3.0) or two-thirds (pH=2.5) of the possible. In addition, it is clear from the parallel (at pH=3.0) or even declining (at pH=2.5) shape of Q-cycle number curves (Fig. 3d,e) that the extent to which the
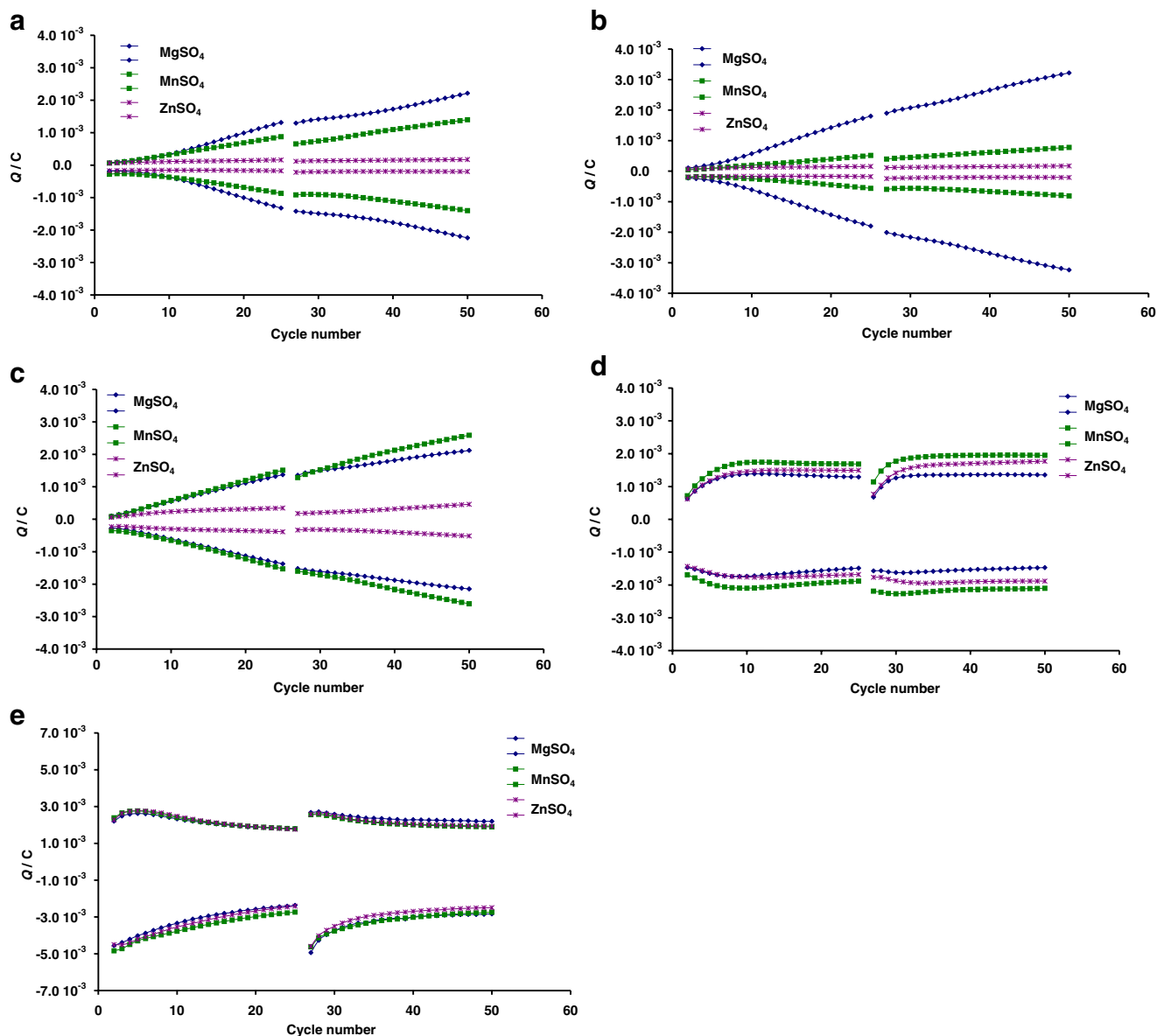
Fig. 3 a Dependence of cathodic and anodic charges on CV cycle number for PPy/SO$_4$ films (3 μm) in different 0.1 M electrolyte solutions, noted in figure, at pH=6.0. **b** Dependence of cathodic and anodic charges on CV cycle number for PPy/SO$_4$ films (3 μm) in different 0.1 M electrolyte solutions, noted in figure, at pH=5.0. **c** Dependence of cathodic and anodic charges on CV cycle number for PPy/SO$_4$ film can be activated using the electrolyte of M^{2+}, is limited. At more neutral solutions (with the pH between 5 and 6), the prolonged cycling of the film in the solution of breaking-in cations seems, at least in certain cases, to allow for better gains. For example, in the solution of MgSO$_4$ at pH=5.0, the cathodic charge of the PPy/SO$_4$ film after 50 electrochemical cycles is ≈85% of the possible. It should be noted that in the solution of monovalent (K$^+$) cations, the received Q-cycle number curves were, independently of pH (3.0 and 6.0), practically coinciding.

PPy/SO$_4$ films (3 μm) in different 0.1 M electrolyte solutions, noted in figure, at pH=4.0. **d** Dependence of cathodic and anodic charges on CV cycle number for PPy/SO$_4$ films (3 μm) in different 0.1 M electrolyte solutions, noted in figure, at pH=3.0. **e** Dependence of cathodic and anodic charges on CV cycle number for PPy/SO$_4$ films (3 μm) in different 0.1 M electrolyte solutions, noted in figure, at pH=2.5

The selection of cations by differences in the charge, size, and deformability of their hydration shell, also by their covalent index and softness values for different types

From our previous results with monovalent cations [8], it became evident that the mobility of the cations in PPy/SO$_4$ films increased in the sequence Li$^+$<Na$^+$<K$^+$<Cs$^+$. This means that less hydrated cations are more mobile in polymer. From the viewpoint of ion size, more restricted mobility is expected in the case of double-charged cations

being more hydrated than single-charged ones. By mechanism, in both cases (single- and double-charged cations) in order to release sulfate ion from the PPy matrix, it must be transferred into a more mobile form by decreasing its charge. In order to do this, an ion pair with a small cation must be formed, after which this pair is able to leave the polymer film. D. G. Leaist et al. [30] have shown that the association of M^+ and SO_4^{2-} ions increases the overall mobility in aqueous solutions and thermodynamic driving forces for their diffusion due to a reduced frictional resistance of merged ions in comparison with two separately diffusing particles. It must be mentioned that the belonging of both the above-given cations (Li^+, Na^+, K^+, Rb^+, Cs^+) and SO_4^{2-} anion to the group of hard acids and hard bases correspondingly causes hard-hard interactions that are primarily electrostatic in nature (i.e., ion pairing) [26].

As concerns the present study with divalent cations, according to [22], the Stokes radii of the cations increase in the following order $Ni^{2+} < Zn^{2+} < Cd^{2+} < Co^{2+} < Mg^{2+} < Mn^{2+}$. Juxtaposing this row with the ability of these ions to break into the film or passivate gives an unexpected result: cations with a larger hydration shell show a better penetration or mobility effect in the PPy film. This may be related to the fact that hydration enthalpy for these cations increases almost in the opposite direction: $Cd^{2+} < Mn^{2+} < Mg^{2+} < Co^{2+} < Zn^{2+} < Ni^{2+}$ [24], which obviously allows for better deformability of the hydration shell of Mn^{2+}, Mg^{2+}, Co^{2+} ions and therefore better mobility as compared with Zn^{2+} and Ni^{2+} ions. In connection with this, Zhang et al. [31] have found that the strength of the interaction between metal cations and the primary shell water molecules in the hexaaqua complexes decreases in the order of $Cd^{2+} > Zn^{2+} > Mg^{2+} (>> Na^+)$ and thus Cd^{2+} and Zn^{2+} ions have a higher tendency to remain in their hexaaqua complex structures compared with Mg^{2+} ions, which may become a restrictive factor in the Cd^{2+} and Zn^{2+} ions' penetration ability. However, the differences in both the hydration numbers (radii) and hydration energies for all the investigated cations seem to be too small to singularly explain this kind of ion behavior.

Besides the metal ion propensity to form ionic bonds (as already discussed above in the case of alkaline metal ions-sulfate complexes), the propensity of multivalent metal ions is also essential to form covalent bonds which are expressible in covalent index values. According to reference [23], this index for M^{2+} increases in the row $Mg^{2+} < Mn^{2+} < Zn^{2+} < Ni^{2+} < Co^{2+} < Cd^{2+}$, generally grouped as break-in promoters or passivation promoters according to their behavior (with the exception of Co^{2+}). Various degrees of covalence, hence the different lengths of cation-anion bonds, is a result of different electron configurations of various divalent cations. Vermaas et al. [32] have analyzed the differences in the electron configuration of the various

divalent cations to give rise preferably to bonds of a covalent or ionic type. Thus, the noble gas outer electron shell structure of Mg^{2+} ions does not favor the formation of covalent bonds, but ionic ones. Mn^{2+} ions with a half-filled d-shell can show anomalies for various properties and behave like Mg^{2+} ions with a full shell, forming ionic bonds. Zn^{2+} and Cd^{2+} ions as cations with a full d-shell are known to form covalent bonds. From the investigation of the structure of the spinels in [32], it was concluded that the degree of bond covalence increased in the following order: $Fe^{2+} < Co^{2+} < Ni^{2+} < Cd^{2+} < Zn^{2+}$, while Mg^{2+} and Mn^{2+} formed ionic bonds. The above-mentioned analysis of metal ion propensity to form ionic or covalent bonds indicates that the metal ions that preferably form ionic bonds (Mg^{2+} and Mn^{2+}) belong to the group promoting break-in but the cations that create covalent bonds (Zn^{2+}, Cd^{2+}, Ni^{2+}) behave as passivating ones. The Co^{2+} ions, though capable to form covalent bonds, cause this (at least in certain cases) less intensively than the three preceding cations. It is worth mentioning that in reference [16], the specific behavior of Co^{2+} was also established in the case of PPy doped with 8-hydroxyquinoline-5-sulfonic acid (PPy/HQS). Thus, the PPy/HQS films were found permeable to cobalt and copper ions but not to nickel ions, despite the fact that the thermodynamic stability of the complexes of these cations with HQS is comparable. These authors suggest that in the case of transition metals, several factors can play a significant role in determining metal ion flux across the polymer film.

As was already mentioned, the cation-anion bond, particularly its strength can be characterized by stability constants of the corresponding complexes. In references [27, 33], the stability constants of the complexes between some divalent metal cations and inorganic anion SO_4^{2-} are given. In reference [27], these constants form the following increasing row: $Mn^{2+} < Mg^{2+} < Sr^{2+} = Ba^{2+} = Fe^{2+} = Zn^{2+} < Ca^{2+} < Ni^{2+} = Cu^{2+} < Co^{2+}$. The stability constant values presented in reference [33] differ somewhat from those previously mentioned (reference [27]) but are mainly in agreement with them. The stability constants of sulfate complexes with M^{2+} are tens of times stronger than those with M^+ [34]. A collation of these rows with the generalized (Irving–Williams stability order) row: $Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+} < Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$, which represents the stability order of divalent cations with a given ligand, once again points to the similarity of Mg^{2+} and Mn^{2+} between them and the difference with Ni^{2+}, Zn^{2+} and Cd^{2+}. As well, this similarity appears in the case of electroreduction of the PPy/SO$_4$ film in the solutions of corresponding M^{2+}. In reference [35], it was also concluded that zinc is very different from magnesium, manganese, and calcium in its heightened binding ability of nitrogen and sulfur. Thus, the stronger the [M^{2+}-SO_4^{2-}] complex is and the more

covalent the bond between the divalent cation and the sulfate anion is, probably causing a more compact and rigid unit, the more suppressed the mobility of a concrete cation or its complex is.

As well from the viewpoint of ion hardness/softness [26], Mg^{2+} and Mn^{2+} ions, likewise alkaline metal ions belong to the group of hard acids and form better mobile ion pairs with hard base SO_4^{2-}. In the case of borderline acids (Co^{2+}, Ni^{2+}, Zn^{2+}) and even more of soft acid (Cd^{2+}), the interaction with hard base SO_4^{2-} decreases the electrostatic effect and increases the covalent bonding effect, resulting in the formation of a less flexible complex with poorer mobility. It is worth noting that in biological media (resembling PPy by the existence of polymeric chains and pyrrole units) where the mobility of Na^+, K^+ have been found to be very high and the mobility of Mg^{2+} and Mn^{2+} have shown semimobile properties, the cations like Ni^{2+} and Zn^{2+} are (usually) static [27].

During the redox cycling of the PPy film, in addition to the factors mentioned above and the mechanism of electro-neutralization (which may be different in the solution of divalent cations, as supposed previously [4, 8]), the pore structure—or channel selectivity factor, must obviously also be taken into account as it becomes essential in the case of biological membrane systems. This means that the flexible polymeric chains (proteins or PPy) can generate gaps (holes) of various sizes and shapes, thus creating a sieving effect by enabling certain ions to be in motion and preventing the motion of others [27, 36]. In this way, also due to the different interaction of different M^{n+} ions with the polymeric chain, the existing "natural" or created by moving (due to externally applied electric field) ions, (micro)porosity of the film possesses discriminative (be-tween size, charge, etc.) properties towards moving ions, i.e., is ion-selective. Though the ion sieving effect seems to be significant according to some of the obtained results (particularly the "contradiction" between the determined porosity/void volume parameters in the PPy/SO_4 film and existence of passivation phenomenon), its proportion remains undetermined.

Summing up the reported and discussed results of our investigation, it appears that the break-in and passivation phenomena in PPy films are the result of many factors, including various physico-chemical properties of dopant and electrolyte ions, and also the pH of the solution. In particular, our results pertaining to the PPy/SO_4 film suggest that the studied specific effects such as break-in or passivation of the film are related to multicharged metal ion propensity to form a M^{2+}-SO_4^{2-} bonding, which is preferably of an electrostatic or covalent type. This propensity originates from different electron configurations of different divalent cations and is reflected in the stability constant values and also in the belonging of these ions to a certain class on the hardness/softness scale. The deform-ability of the hydration shell of the cation seems to have an effect greater than the size of M^{2+} ions does on the ion mobility in PPy films. This is a feature of importance that at lower pH values, the restructuring of the PPy matrix abolishes the passivation phenomenon and homogenizes the influence of different cations on the investigated break-in phenomenon.

Conclusions

It was found that from among the studied M^{2+}, two different types of cations were found: Mg^{2+}, Mn^{2+}, and Co^{2+} cause the break-in phenomenon in PPy films, while Ni^{2+}, Zn^{2+}, and Cd^{2+} bring about the passivation of PPy films.

The above-mentioned phenomena appear clearly only at pH>4.0; at pH=3.0 and particularly at pH=2.5, the dependencies of cathodic and anodic charges on the CV cycle number are closely coinciding for the cations of different types, indicating the changed polymeric structure.

The extent of the break-in effect (increase of charges with the cycle number) on a certain cation depends on the pH value. The ability of different M^{2+} to promote this effect at different pH values can also vary.

Certain correlations have been drawn between some physico-chemical parameters of the ions, such as the size and deformability of their hydration shell as well as their covalent index and softness, and the investigated break-in and passivation phenomena. It seems that the stronger (more stable) the [M^{2+}-SO_4^{2-}] complex is and the more covalent the bond between its components is, the more suppressed the mobility of a concrete cation or its complex is.

The possible role of ion sieving effect, caused by the different selectivity of PPy chains and pores towards the cations of different nature, on the extent of bound/trapped cations in polymeric structure, was discussed.

References

1. Inzelt G (1989) Electrochim Acta 34:83
2. Pei Q, Inganäs O (1993) J Phys Chem 97:6034
3. Gandhi MR, Murray P, Spinks GM, Wallace GG (1995) Synth Met 73:247
4. Tamm J, Hallik A, Alumaa A, Sammelselg V (1997) Electrochim Acta 42:2929
5. Lee H, Yang H, Kwak J (1999) J Electroanal Chem 468:104
6. Hallik A, Alumaa A, Sammelselg V, Tamm J (2001) J Solid State Electrochem 5:265
7. Fernández Romero AJ, López Cascales JJ, Otero TF (2005) J Phys Chem B 109:21078
8. Tamm J, Alumaa A, Hallik A, Johanson U, Tamm L, Tamm T (2002) Russ J Electrochem 38:182

9. Iseki M, Saito K, Ikematsu M, Sugiyama Y, Kuhara K, Mizukami A (1993) J Electroanal Chem 358:221
10. Inzelt G, Kertész V, Nybäck AS (1999) J Solid State Electrochem 3:251
11. Li Y, Qian R (1993) J Electroanal Chem 362:267
12. Alumaa A, Hallik A, Mäeorg U, Sammelselg V, Tamm J (2004) Electrochim Acta 49:1767
13. Weidlich C, Mangold K-M, Jüttner K (2005) Electrochim Acta 50:1547
14. Hallik A, Alumaa A, Tamm J, Sammelselg V, Väärtnõu M, Jänes A, Lust E (2006) Synth Met 156:488
15. Gohil GS, Binsu VV, Shahi VK (2006) J Membr Sci 280:210
16. Misoska V, Ding J, Davey JM, Price WE, Ralph SF, Wallace GG (2001) Polymer 42:8571
17. Reece DA (2003) Development of conducting polymers for separations. PhD Thesis, University of Wollongong
18. Iseki M, Saito K, Kuhara K, Mizukami A (1991) Synth Met 40:117
19. Yakovleva AA (2000) Russ J Electrochem 36:1275
20. Partridge AC, Milestone C, Too CO, Wallace GG (1997) J Membr Sci 132:245
21. Davey JM, Ralph SF, Too CO, Wallace GG (1999) Synth Met 99:191
22. Marcus Y (1997) Ion properties. Marcel Dekker, New York
23. McCloskey J, Newman MC, Clark SB (1996) Environ Toxicol Chem 15:1730
24. Krestov GA (ed) (1987) Ionnaya Solvatatzya. Nauka, Moskva
25. Hallik A, Alumaa A, Kurig H, Jänes A, Lust E, Tamm J (2007) Synth Met 157:1085
26. Available at http://andrew.ucsd.edu/courses/sio263/ClassNotes/3.pdf
27. Fraústo da Silva JJR, Williams RJP (2004) The biological chemistry of the elements—the inorganic chemistry of life (part 1). Oxford University Press, Oxford
28. Zhang X, Bai R (2003) Langmuir 19:10703
29. Deslouis C, El Moustafid T, Musiani MM, Tribollet B (1996) Electrochim Acta 41:1343
30. Leaist DG, Goldik JS (2001) J Solution Chem 30:103
31. Zhang Y-H, Chan CK (2002) J Phys Chem A 106:285
32. Vermaas FHC, Schmidt ER (1959) Beitr Mineral Petrogr 6:219, http://www.springerlink.com/content/r67312rpv4020171/fulltext.pdf
33. Janoš P (1993) J Chromatogr A 657:435
34. Daniele PG, Rigano C, Sammartano S (1982) Inorg Chim Acta 63:267
35. Glusker JP, Katz AK, Bock CW (1999) Rigaku J 16:8
36. Elinder F, Århem P (2004) Q Rev Biophys 36:373