

György Inzelt · Vilmos Kertész · Ann-Sofi Nybäck

## Electrochemical quartz crystal microbalance study of ion transport accompanying charging-discharging of poly(pyrrole) films

Received: 21 August 1998 / Accepted: 21 October 1998

**Abstract** Electrochemical quartz crystal microbalance studies on poly(pyrrole) electrodes revealed a complex nature of the potential-dependent sorption of ionic substances. It is found that the relative contribution of anions and cations to the overall charge transport process depends upon several factors, such as the oxidation state of the polymer, the composition of the supporting electrolyte as well as on the film thickness. The phenomena observed are discussed in terms of morphological transformations arising as a result of interactions between the polymer and the mobile substances.

**Key words** Poly(pyrrole) · Electrochemical quartz crystal microbalance · Ionic charge transport

### Introduction

Conducting polymers prepared by oxidative electropolymerization or by chemical oxidation from simple, inexpensive monomers, such as pyrrole, aniline or thiophene, have been in the foreground of research activity in the last two decades [1–3]. There are at least two major reasons for this intense interest. First is intellectual curiosity of scientists that focuses on understanding the behaviour of these systems, in particular on the mechanism of charge transfer and charge transport processes occurring in the course of redox reactions of conducting polymeric materials. Second is the wide range of promising applications in the field of energy storage, electrocatalysis, organic electrochemistry and

bioelectrochemistry, photoelectrochemistry, electroanalysis, electrochromic displays, electronic devices and corrosion protection of metals and semiconductors.

Poly(pyrrole) (PPy) is, perhaps, the most widely studied conducting polymer [1–34]. It can easily be synthesized both in aqueous [8–11, 20, 27, 28, 31] and nonaqueous [4, 5, 10–12, 16, 20] solutions. It is stable – at least in a relatively wide potential range [5, 14] – during thousands of charge-discharge cycles and, under properly selected conditions, its response is fast. In contrast to poly(aniline), it can operate both in acidic and neutral solutions, which makes the poly(pyrrole) electrode attractive for use as a sensor component in bioelectroanalytical chemistry. Practically, in all applications the ionic diffusion must be sufficiently fast so that the device responds in a reasonably short time. Understanding the role of the ionic species involved in the charge compensation process is of utmost importance. It cannot be deduced from the electrochemical response of the polymer film electrode because it does not contribute directly to the measured current. The trivial approach – as it was assumed in the early works [1] – is that the counterions (anions) enter or leave the film during electrochemical oxidation or reduction of the polymer. It has, however, become clear that the mechanism is more complex and the behaviour of the polymer is affected not only by the anions but also by the cations present. The use of several in situ techniques, such as piezoelectric microgravimetry at an electrochemical quartz crystal microbalance (EQCM) [6, 15, 17–20, 23, 29], radiotracer methods [9], probe beam deflection (PBD) [22, 24], scanning electrochemical microscopy (SECM) [27], X-ray emission analysis [20] and Rutherford backscattering spectrometry (RBS) [28], has provided evidence that cations also participate in the ion transport. Because the relative contribution of anions and cations to the overall charge transport significantly depends upon the nature of both co-ions and counterions as well as the oxidation state (electrode potential), the reported results are subject to controversies [1, 6, 13, 17–24, 30, 34].

G. Inzelt(✉) · V. Kertész  
Department of Physical Chemistry,  
Eötvös Loránd University,  
P.O. Box 32, H-1518 Budapest 112, Hungary

A.-S. Nybäck  
Laboratory of Analytical Chemistry,  
Abo Akademi University,  
Biskopsgatan 8, FIN-20500 Abo, Finland

In the present paper, we report our results of the systematic study on the ionic charge transport accompanying the redox processes of a PPy film. An EQCM was used to follow the changes of the surface mass. EQCM was chosen because piezoelectric microgravimetry at an EQCM is one of the most powerful techniques used to monitor sorption-desorption processes occurring in the polymer films. In order to gain better understanding of the phenomenon in question, PPy electrodes of different thicknesses have been prepared and characterized in contact with various electrolytes (anion-cation combinations).

Only selected results will be presented in order to illustrate the most important features of the anion and cation transports, as well as the effect of the film thickness on this transport.

## Experimental

The EQCM system described previously was used [35, 36]. Five and ten megahertz AT-cut crystals were used. Each side of the crystals was coated with gold or platinum. The crystals were mounted in a suitably formed part of the cylindrical holder made from Teflon. This holder also contained the oscillator circuit which was isolated from the solution. Only one side of the crystals, that served as a working electrode, was exposed to the electrolyte solution. The connections to the metal coatings of both sides of the crystals were made with a gold foil. This arrangement allowed us to use the crystal as a plate working electrode (projected area  $0.4 \text{ cm}^2$ ). Linearity of the relation between the resonance frequency and the change of the surface mass was checked by the usual calibration procedure and also by depositing PPy films of different thicknesses. A linear relationship between the frequency change ( $\Delta f$ ) caused by deposition of PPy films (0.2–40 kHz) and the charge transferred ( $\Delta Q$ ) during the oxidation/reduction of the polymer was found. The Sauerbrey equation with an integral sensitivity of the crystal [ $C_f = 2.264 \times 10^8 \text{ Hz cm}^2 \text{ g}^{-1}$  (10 MHz) and  $C_f = 5.56 \times 10^7 \text{ Hz cm}^2 \text{ g}^{-1}$  (5 MHz)] was used to calculate the mass change ( $\Delta m$ ) from the frequency change. A Pt wire was used as the counter electrode. The reference electrode was a saturated sodium chloride calomel electrode (SCE).

All chemicals were of analytical grade (Merck) and were used as received, except pyrrole that was distilled and stored in the dark under an argon atmosphere. All aqueous solutions were prepared with triply distilled, deionized water. The solutions were purged with oxygen-free nitrogen before use and an inert gas blanket was maintained throughout the experiments. The poly(pyrrole) films were prepared by using 0.1 M pyrrole in 0.1–1 M supporting electrolytes under continuous cycling between  $-0.3$  and  $0.8 \text{ V}$  (SCE) at different scan rates ranging from 10 to  $100 \text{ mV s}^{-1}$ . Films of different thicknesses were obtained by varying the number of cyclic voltammetry cycles and the sweep rate.

The thickness of the films was estimated by considering the projected area of the electrode, the density of the film ( $1.5 \text{ g cm}^{-3}$ ) [4] and the “dry” mass of the polymer film. The dry mass was calculated from the frequency change caused by deposition of the PPy films, i.e., the EQCM system containing the electrode covered with PPy was removed from the cell, dried and then the frequency value was measured in air. The dry mass was obtained from the difference of the resonant frequency of loaded and unloaded crystals. An estimation was also made from the charge transferred during the redox reaction, assuming that the oxidation degree of the polymer is equal to 0.25, i.e., one electron per four pyrrole units. Somewhat surprisingly, the thickness values calculated from the charge and frequency measurements, respectively, did not differ significantly; the deviation usually was less than 10–30%. However, these thickness values can be used only for comparison of different

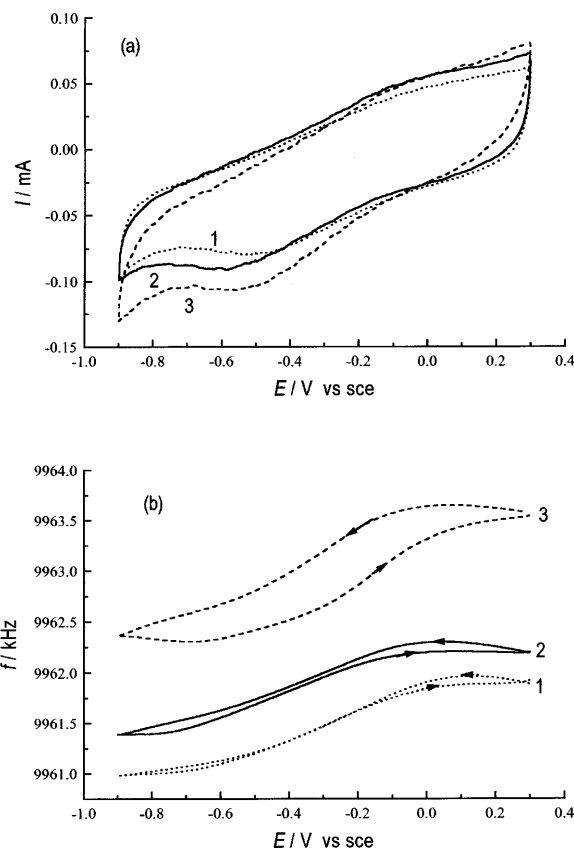
films because in contact with solution the PPy films swell [18] and their volume increases greatly during oxidation (about 40–50%) [30]; also the actual charge for doping depends on the experimental conditions [15]. Nevertheless, our results are in good accord with the literature values,  $3\text{--}4 \mu\text{m cm}^{-2} \text{ C}^{-1}$ , estimated by using the charge passed during film deposition and an apparent  $n$  value of 2.25 for the formation reaction [4, 5, 10, 19, 20, 28, 31, 34]. The direct thickness measurements by applying profilometers [5, 26] and scanning electron microscopy [20], respectively, have confirmed that these estimates give useful thickness values.

The supporting electrolyte used for preparation and characterization was systematically varied, e.g., in case of the study of the cation effect, the same anion was used. After changing the electrolyte, the electrode was washed, soaked in the new solution for ca. 10 min and then 10–15 potential cycles were executed in order to replace completely the ions incorporated in the film during the preceding experiments. Then, three cyclic voltammograms were registered. In general, the second cycles are compared in order to avoid the “first cycle effect” [1].

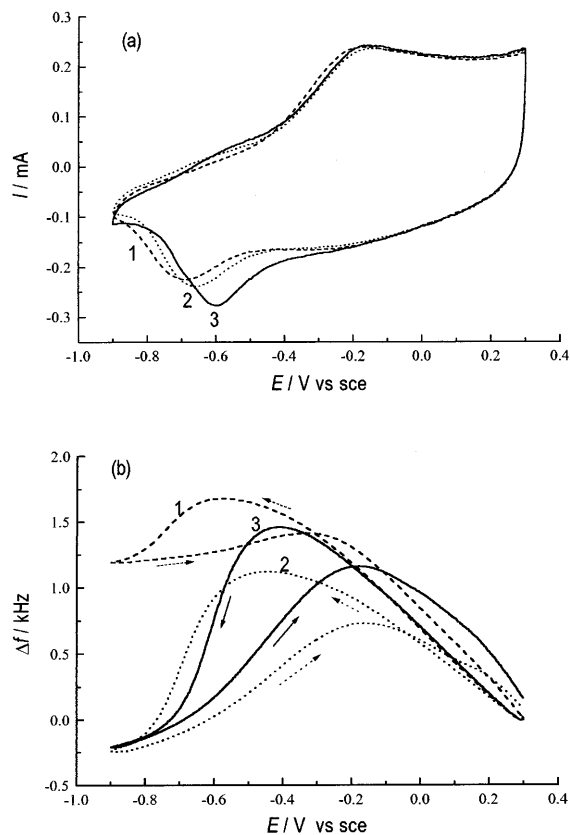
An Electroflex 451 potentiostat and Philips universal frequency counter PM6685 connected to a personal computer was used for the control of the measurements and for data collection.

## Results and discussion

Figures 1–3 clearly illustrate the problem why some researchers argued that insertion and expulsion of anions



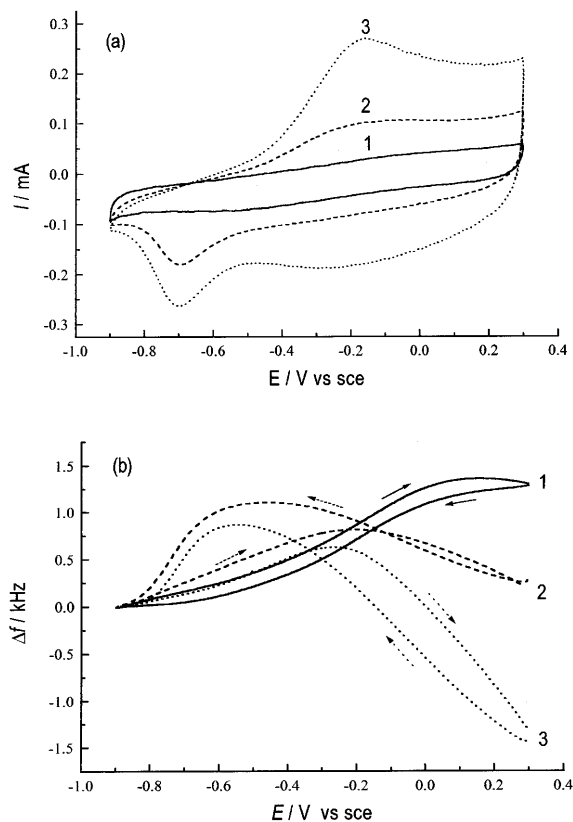
**Fig. 1** Effect of univalent cations on the cyclic voltammetric (a) and EQCM (b) responses of a thin ( $L \approx 0.1 \mu\text{m}$ ) poly(pyrrole) (PPy) film electrodeposited on Au in contact with aqueous solutions of  $1 \text{ mol dm}^{-3}$  1 LiCl, 2 NaCl and 3 KCl. Potential scan rate (v):  $10 \text{ mV s}^{-1}$



**Fig. 2** Effect of univalent cations on the cyclic voltammetric (a) and EQCM (b) responses of a thick ( $L \approx 0.62 \mu\text{m}$ ) PPy film electrodeposited on Au. Other conditions and markings as in Fig. 1

is the dominant ionic transport over that of cations [8–12, 19, 21, 23, 28, 30–34] while others claimed the opposite transport predominates [6, 22], especially in presence of large, i.e., less mobile, counterions (anions) [34]. This ion-size dependent switching from anion to cation transport has been demonstrated [17, 19, 27, 28, 34]. Besides the size exclusion and slow diffusion (migration), interaction forces play an important role. There may be specific interactions between the polymer (neutral or charged) and the ions (as well as other components of the electrolyte solution), i.e., ion selectivity or, which is more plausible, large size anions used during the electropolymerization, sometimes polymeric, are trapped owing to additional van der Waals and electrostatic forces.

The EQCM data shown in Figs. 1–3 reveal that the relative contribution of anions and cations to the overall charge transport depends on the film thickness, even if small-size ions are used. The cyclic voltammograms do not relate to this phenomenon. The frequency (mass) changes can be rationalized as follows. In the case of thin films, cation expulsion accompanies oxidation of the polymer, while for thick films, the incorporation of anions will be dominant at higher positive potentials, at least if PPy films are in contact with aqueous solutions containing chloride salts of alkali-metal cations. Al-



**Fig. 3** Effect of thickness on the cyclic voltammetric (a) and EQCM (b) responses of the Au/PPy films. The film thicknesses are  $l$  ca. 0.14, 2 0.48 and 3 0.96  $\mu\text{m}$ , respectively. Solution: 1 M NaCl;  $\nu = 10 \text{ mV s}^{-1}$ . For the sake of clarity, only the frequency changes and not the frequency values are displayed

though such a conclusion seems reasonable, the calculation of the mass change as a function of charge transferred reveals that a flux and counterflux of solvent molecules should be taken into account – considering the motion of hydrated ions or just solvent swelling of the film – and the transfer of salts cannot be excluded [1, 37] either. In addition, an interplay between the elastic and viscoelastic behaviour may take place if extensive swelling occurs [18]. All these phenomena may depend not only upon the oxidation level of PPy but also upon the electrolyte concentration.

Although a deviation from the elastic response may be expected [18], i.e., a calculation based on the Sauerbrey equation may result in somewhat incorrect data, the effect observed cannot be assigned to this artifact. The magnitude of the mass change is reasonable, i.e., for thick films the mass changes accompanying the redox transformation of the film are proportional to the dry thickness and the charge transferred, and no substantial deviation can be observed (e.g., see curves 2 and 3 in Fig. 3). A similar proportionality has been observed between the frequency decrease, caused by the deposition of the film, and the film swelling, i.e., between the frequency change related to the dry polymer and that of the polymer in contact with the solution. Even the swelling of a thick film was more extensive, in accord

with previous observations for poly(o-phenylenediamine) films [38].

In the former EQCM study of poly(pyrrole) films in contact with aqueous solutions of chloride salts of alkali metals ( $c = 0.1 \text{ mol dm}^{-3}$ ), both cation ejection and anion injection were observed at low and high potentials, respectively, during oxidation. The opposite transport was observed during the film reduction [19]. The participation of cations was more pronounced in the case of  $\text{Cs}^+$  cations, with a smaller effect observed for  $\text{K}^+$  and  $\text{Li}^+$  cations. Relatively thick ( $d = 0.5 \text{ }\mu\text{m}$ ) films were investigated, but no thickness dependence of the ion transport was studied. The difference in the extent of permselectivity was explained by the effect of the ion's size and the interactions between the ions and the polymer. Neither solvent nor salt transport was considered [19].

Although such assumptions may be accepted to interpret the so-called non-permselective behaviour, neither these assumptions nor any sound thermodynamic theory [37] can provide an explanation of the thickness dependence. It is, most likely, due to the polymeric nature of these surface films and not to the chemical properties of the polymer and ions that play the determining role in the extent of the interaction, beside the coulombic forces. The versatility of the phenomenon can be related to changes in the morphology of the polymer network that is very sensitive to the environmental conditions (nature and concentration of the electrolyte, solvent and temperature).

According to the theory of metastable adsorption of de Gennes [39, 40], the density of the polymer layer decreases with the increase of distance from the electrode surface. That is, the concentration of charged sites also changes, i.e. it may be assumed that all interactions can and must be described by certain distribution functions. The minimum of the free energy is established as the result of partial interaction energies including polymer-solvent, polymer-ion, ion-ion, polymer-polymer, ion-solvent interactions, ionic shielding, etc., in a rather complex manner. If the cation and anion transport could take place within the film in a concurrent manner, then cation transport was more significant for thin films, where a more compact structure predominates, so at least a qualitative elucidation of the phenomena observed can be given. It should be emphasized that the motion of all mobile components (anions, cations and solvent molecules) may occur at each potential, disregarding the film thickness. This motion is manifested by a somewhat smaller molecular mass of the respective anions or cations than the apparent molecular mass that can be calculated from the ratio of the frequency change (by using the Sauerbrey equation) and charge in the potential range where the  $\Delta f$  versus  $\Delta Q$  plots are linear. This apparent discrepancy indicates that cation desorption and anion sorption occur simultaneously in the course of oxidation, although the solvent flux should not be neglected, either.

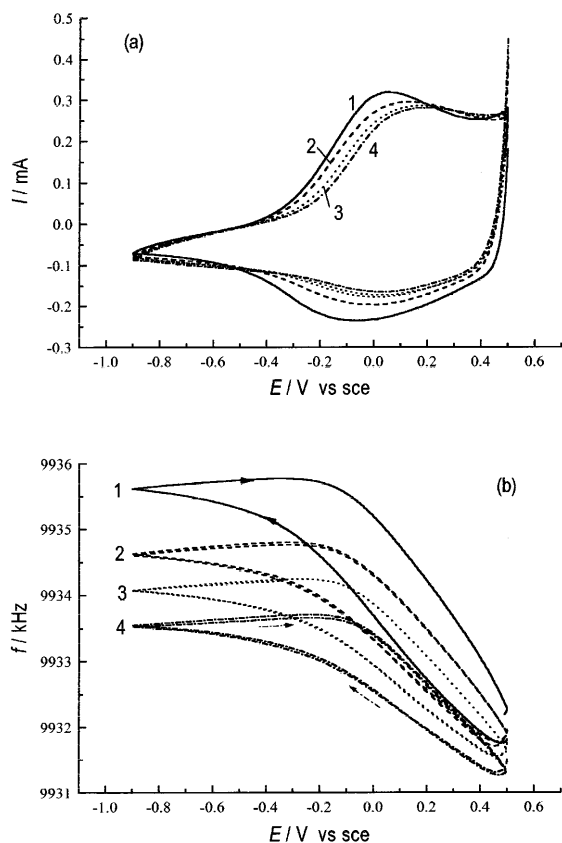
An alternative or complementary explanation can be also given, based on Feldberg's model [41]. In this

model, it is suggested that the double layer capacity linearly increases with an increase of the fraction of the polymer converted to its oxidized (conducting) form. It may be assumed that mostly anions participate in the formation of the electrical double layer at potentials more positive than the potential of zero charge ( $E_{\text{pzc}}$ ). It can be seen in Figs. 2 and 3 that the frequency decrease (i.e., mass increase), that can be assigned to ingress of the anions, occurs mostly in the capacity range.

Tanguy et al. [42] also analyzed the problem of the capacity current. Their explanation contrasts with Feldberg's model which assumes that differential capacity is potential independent. The results of the impedance measurements indicate the existence of two types of ion trapping sites in the PPy films. The number of the deeply trapped ions, whose motion lags behind the ac signal, increases during the film charging. That is, a small number of ions that have entered the film remains in a quasi-free state. Near the redox potential, the number of quasi-free ions is at maximum, resulting in a maximum film capacity. In this interpretation, there are two types of current in cyclic voltammetry. Namely, there is a capacity current without a hysteresis effect and a noncapacitive current arising from the deeply trapped ions. Transport of the latter ions results in a large hysteresis that is responsible for broadening of the electroreduction peak. It is reasonable to assume that either the increase of the capacity due to the larger surface area and consequently the larger accumulation of anions may cause the effect observed (due to the morphological changes, i.e., in the case of thicker films a less compact structure prevails) or the ratio of deeply trapped ions increases in the more loose structure that may explain the more pronounced hysteresis observed for thick films (Figs. 2 and 3).

However, conformational structural changes have also to be considered in the course of oxidation of PPy films. In neutral (reduced) poly(pyrrole), owing to the attractive interactions between neighbouring chains, a compact and closed polymer structure develops. In the course of oxidation the effect of repulsive Coulombic forces will become stronger and the concomitant conformational movements of polymer chains promote increasing interchain distances [30]. Within the framework of this model [30] it is not surprising that in the early phase of oxidation of thick PPy films the transport of cations dominates similarly to that observed for thin films having a more compact structure.

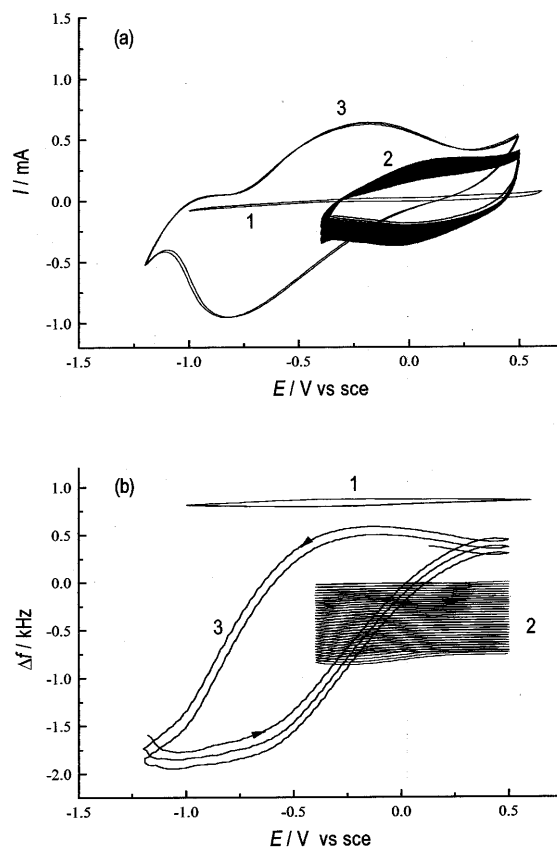
Because the ratio of the anionic to cationic charge transport depends upon the nature of mobile ions, a series of experiments have been carried out in the presence of bivalent cations as well as for different anions while using the same cations. Figure 4 shows cyclic voltammograms and simultaneously recorded EQCM frequency changes for a PPy film in contact with 0.1 M aqueous solutions of chloride salts of alkali-earth metal cations. A characteristic shift of the peak potentials was observed, indicating an interaction between the cations and the polymer. This interaction increases in the order



**Fig. 4** Effect of bivalent cations on the cyclic voltammetric (a) and EQCM (b) responses of a thick ( $L \approx 1.35 \mu\text{m}$ ) Au/PPy film in contact with aqueous solutions of  $0.1 \text{ mol dm}^{-3}$  1  $\text{MgCl}_2$ , 2  $\text{CaCl}_2$ , 3  $\text{SrCl}_2$  and 4  $\text{BaCl}_2$ ;  $\nu = 10 \text{ mV s}^{-1}$

of  $\text{Ba}^{2+} < \text{Sr}^{2+} < \text{Ca}^{2+} < \text{Mg}^{2+}$ . The film electroactivity and mass also increase in the same order. At the early stage of oxidation, i.e., at low potential values, a slight frequency increase can be observed. This increase is practically independent of the nature of the cations. From the  $\Delta f$  versus  $\Delta Q$  plot, a value of the molar mass of 1–3 can be calculated which – within experimental error – is close to the molecular mass of the hydrogen ion. Even in neutral solutions, a partial deprotonation of pyrrole groups is plausible during injection of positive charges to the polymer chains. However, this slight mass decrease may also be assigned to the simultaneous motion of ions and solvent molecules in the opposite direction. At more positive potentials, a continuous decrease of frequency was observed in all solutions studied. The molecular mass calculated was  $35 \pm 5$  for all systems, independently of the nature of cations. Therefore, a conclusion may be drawn that chloride ions enter the film to compensate for the excess charge of the polymer. In chloride solutions, there was no loss of the film electroactivity that has been observed in sulfate solutions of doubly charged metal cations [33]. Specific interactions between the PPy film and sulfate ions has been proved by radiotracer experiments [9]. It has also been verified that there is no significant embedment of chloride anions, in

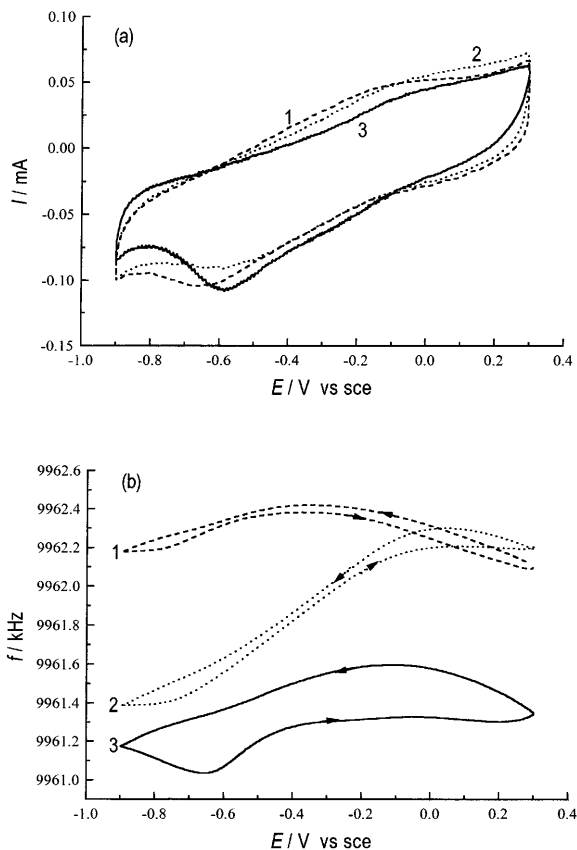
contrast to sulfate anions [9]. After exchanging the chloride for sulfate anions, however, the PPy film became passive in the presence of bivalent cations, as shown in Fig. 5. The PPy film was prepared in  $0.1 \text{ M}$   $\text{CaCl}_2$  electrolyte and investigated in  $\text{MeCl}_2$  solutions (Fig. 4). By replacing  $\text{MgCl}_2$  for  $\text{MgSO}_4$  we did not observe practically any current on mass change (curves 1 in Fig. 5a and 5b). This effect was assigned to morphological transformations resulting in a densely packed structure [33]. This structure might be related to condensation of co-ions enhanced by the presence of strongly bounded counterions. This effect depends upon the electrolyte concentration and also on the film thickness. Therefore, its origin might be certainly attributed to the polymeric nature and polyelectrolyte behaviour of the surface PPy films. This explanation is supported by the fact that in acidic solutions the film can be activated. An exchange of  $\text{MgSO}_4$  for  $0.1 \text{ M}$   $\text{H}_2\text{SO}_4$  causes a gradual increase of current and the respective mass change (curves 2 in Fig. 5 a and 5b). This continuous increase of the surface mass during cycling indicates that the film swells. In accordance with the previous observations, the decrease of pH causes an



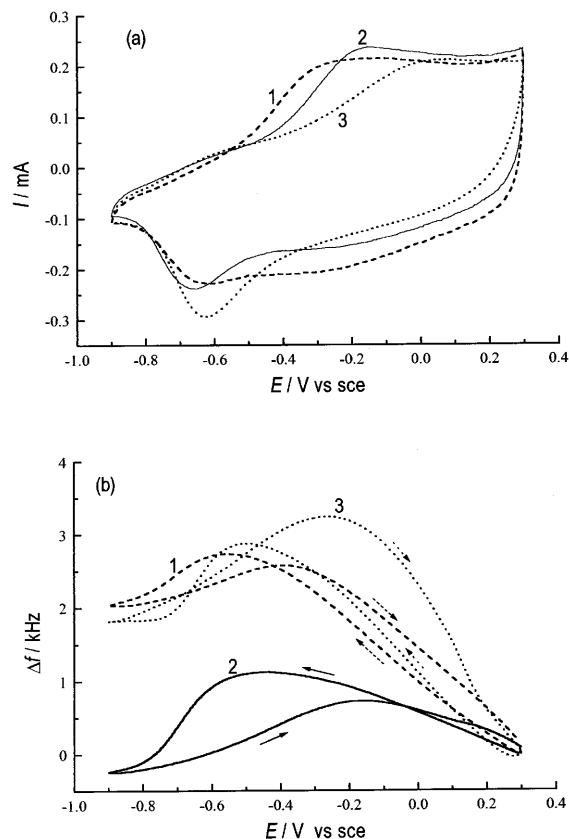
**Fig. 5a, b** Effect of sulfate ions on the electrochemical activity of a PPy film ( $L \approx 0.15 \mu\text{m}$ ) in presence of a bivalent cation. Cyclic voltammetric (a) and EQCM (b) responses after replacing of  $0.1 \text{ M}$   $\text{MgCl}_2$  by  $0.1 \text{ M}$   $\text{MgSO}_4$  1, reactivation in  $0.1 \text{ M}$   $\text{H}_2\text{SO}_4$  solution 2 and the behaviour of the activated film in contact with  $0.1 \text{ M}$   $\text{NaCl}$  3. Potential scan rate:  $50 \text{ mV s}^{-1}$

increase of electroactivity of the polymer owing to the larger ion diffusion coefficient for the more open, swollen film structure. After this activation, the film shows the expected behaviour in NaCl electrolyte (curves 3 in Fig. 5 a and b).

The influence of counterions is investigated by using sodium salts of various anions. Figures 6 and 7 illustrate the effect of anions on the cyclic voltammetric and EQCM responses for two different film thicknesses. The shift of the cyclic voltammetric curves (peak potentials) in the presence of different anions indicates that the interaction between the anions and the polymer increases in the order of  $\text{ClO}_4^- < \text{Cl}^- < \text{NO}_3^-$ . It may be reasonably assumed that different film morphologies developed in the presence of different anions [13, 30, 33], and consequently the sorption-desorption processes of mobile substances are determined by the compactness of the film and by the specific interactions of the polymer sites and ions. Noticeably, the interactions and the film structure depend upon the potential, i.e., on the charging level. In light of these considerations, it is not surprising that the potential-dependent relative contributions of anions and cations to the overall ion exchange process depend on the nature of the anions, as can be seen in Figs. 6 and 7. The “thickness effect” appeared also in



**Fig. 6** Effect of anions on the cyclic voltammetric (a) and EQCM (b) responses of a thin ( $L \approx 0.12 \mu\text{m}$ ) PPy film on Au in contact with aqueous solutions of  $1 \text{ mol dm}^{-3}$  1  $\text{NaNO}_3$ , 2  $\text{NaCl}$  and 3  $\text{NaClO}_4$ ;  $v = 10 \text{ mV s}^{-1}$



**Fig. 7** Effect of anions on the cyclic voltammetric (a) and EQCM (b) responses of a thick ( $L \approx 0.52 \mu\text{m}$ ) PPy film on Au. Other conditions and markings as in Fig. 6

this case and, obviously, it depends also upon the composition of the electrolyte. Importantly, even the extent of swelling of the reduced, i.e., “neutral”, film depends on the nature and concentration of the supporting electrolyte, from similar behaviour of other electrochemically active polymer films [38, 43]. For a thin film (Fig. 6), swelling is much more extensive if the film is in contact with perchlorate solution rather than chloride and especially nitrate solutions. For a thick film, this order is different. This swelling phenomenon may be also related to the film morphology.

## Conclusions

The results of the EQCM experiments confirm that both anions and cations participate in the overall ionic charge transport during the redox electrochemistry of poly(pyrrole) films. The relative contribution of different substances to the solution-polymer charge exchange varies as a function of potential, i.e., with the degree of oxidation of PPy, and depends upon the nature and concentration of the electrolyte solution as well as the film thickness. The data presented indicate also that films swell extensively. The phenomena observed may be

explained by changes of the film morphology resulting from interactions between the polymer and mobile species (ions and solvent molecules). Our study sheds some light on the origin of the apparent contradictions in the literature results on the role of ionic sorption in the electrochemistry of poly(pyrrole) film coated electrodes.

**Acknowledgements** Financial support of the Hungarian Scientific Research Fund (OTKA-TO14928), at the Ministry of Culture and Education (MKM 379/95 and FKFP-015/97), as well as the travel expenses (A.-S.N.) covered by the exchange programme between the Finnish and Hungarian Academy of Sciences are gratefully acknowledged.

---

## References

- Inzelt G (1994) Mechanism of charge transport in polymer-modified electrodes. In: Bard AJ (ed) *Electroanalytical chemistry*, vol 18. Dekker, New York, pp 89–241
- Lyons MEG (ed) (1994) *Electroactive polymer electrochemistry*, part 1. Plenum Press, New York
- Lyons MEG (ed) (1996) *Electroactive polymer electrochemistry*, part 2. Plenum Press, New York
- Diaz AF, Castillo JI, Logan JA, Lee WY (1981) *J Electroanal Chem* 129: 115
- Bull RA, Fan FRF, Bard AJ (1982) *J Electrochem Soc* 129: 1009
- Kaufman JH, Kanazawa KK, Street GB (1984) *Phys Rev Lett* 53: 2461
- Mengoli G, Musiani MM, Fleischmann M, Pletcher D (1984) *J Appl Electrochem* 14: 285
- Mermilliod N, Tanguy J, Petiot F (1986) *J Electrochem Soc* 133: 1073
- Inzelt G, Horányi G (1987) *J Electroanal Chem* 230: 257
- Paulse CD, Pickup PG (1988) *J Phys Chem* 92: 7002
- Vork FTA, Janssen LJJ (1988) *Electrochim Acta* 33: 28
- Panero S, Prospero P, Passerini S, Scrosati B, Perlmutter DD (1989) *J Electrochem Soc* 136: 3729
- Vork FTA, Schuermans BCAM, Barendrecht E (1990) *Electrochim Acta* 35: 567
- De Paoli MA, Panero S, Prospero P, Scrosati B (1990) *Electrochim Acta* 35: 1145
- Baker CK, Qiu YJ, Reynolds JR (1991) *J Phys Chem* 95: 4446
- Novák P, Rasch B, Vielstich W (1991) *J Electrochem Soc* 138: 3300
- Naoi K, Lien M, Smyrl W (1991) *J Electrochem Soc* 138: 440
- Muramatsu H, Ye X, Suda M, Sakuhara T, Ataka T (1992) *J Electroanal Chem* 322: 311
- Bose CSC, Basak S, Rajeshwar K (1992) *J Phys Chem* 96: 9899
- Duffitt GL, Pickup PG (1992) *J Chem Soc Faraday Trans* 88: 1417
- Sabatini E, Ticianelli E, Redondo A, Rubinstein I, Rishpon J, Gottesfeld S (1993) *Synth Met* 55–57: 1293
- Novak P, Kotz R, Haas O (1993) *J Electrochem Soc* 140: 37
- Schmidt VM, Heitbaum J (1993) *Electrochim Acta* 38: 349
- Lopez C, Mendes Viegas MF, Bidan G, Vieil E (1994) *Synth Met* 63: 73
- Paasch G, Scheisser D, Bartl A, Naarmann H, Dunsch L, Göpel W (1994) *Synth Met* 66: 135
- Amemiya T, Hashimoto K, Fujishima A (1994) *J Electroanal Chem* 377: 143
- Arca M, Mirkin MV, Bard AJ (1995) *J Phys Chem* 99: 5040
- Wainright JS, Zorman CA (1995) *J Electrochem Soc* 142: 384
- Naoi K, Oura Y, Maeda M, Nakamura S (1995) *J Electrochem Soc* 142: 417
- Otero TF, Grande HJ, Rodríguez J (1997) *J Phys Chem* 101: 3688
- Yang H, Kwak J (1997) *J Phys Chem* 101: 4656
- Warren LF, Anderson DP (1987) *J Electrochem Soc* 134: 101
- Tamm J, Hallik A, Alumaa A, Sammelseg V (1997) *Electrochim Acta* 42: 2929
- Jüttner K, Ehrenbeck C (1998) *J Solid State Electrochem* 2: 60
- Inzelt G (1993) *J Electroanal Chem* 348: 465
- Inzelt G, Kertész V, Láng G (1993) *J Phys Chem* 97: 6104
- Pater E, Bruckenstein S, Hillman AR (1996) *J Chem Soc Faraday Trans* 92: 4087
- Martinusz K, Czirok E, Inzelt G (1994) *J Electroanal Chem* 379: 437
- de Gennes PG (1981) *Macromolecules* 14: 1637
- de Gennes PG (1985) *CR Acad Sci Paris* 301: 1399
- Feldberg SW (1984) *J Am Chem Soc* 106: 4671
- Tanguy J, Mermilliod N, Hoclet M (1987) *J Electrochem Soc* 134: 795
- Kertész V, Bácskai J, Inzelt G (1996) *Electrochim Acta* 41: 2877