The mechanism of electrode passivation during the electrodeposition of polypyrrole from aqueous solutions containing fluoride anions

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Abstract

The electrodeposition of polypyrrole from an aqueous solution containing a fluoride salt as supporting electrolyte is associated with a self-passivation of the electrode, caused by an unusually low conductivity of the polymer. Conductivity values are deduced from impedance data and from a special analysis of the cyclovoltammograms recorded during the potentiodynamic synthesis. Ion exchange experiments, the deposition from mixed KF/KCl electrolytes as well as the completely different behaviour during poly(N-methylpyrrole) deposition lead to the conclusion that the positive charges in oxidized polypyrrole fluoride films are not located on the polymer backbone, but on the hydrogen atom of the pyrrole nitrogen. This system is stabilized by hydrogen bonds to the fluoride ion. © 1998 Elsevier Science S.A. All rights reserved.

1. Introduction

It is now widely accepted that the main polymerization path of pyrrole involves the oxidation of monomers and of intermediate oligomers to radical cations. The radical cations combine to a positively charged ion, which is non-radical. As a final step, a deprotonation to a neutral molecule can occur. However, the longer the oligomer (polymer) chain, the lower is the oxidation potential.

The electrodeposition of these polymers and their physicochemical properties strongly depend on the concentration and the kind of the used supporting electrolyte whose electrolyte anion is incorporated into the growing polypyrrole as counter ion for the compensation of the positively charged polymer backbone, and whose concentration c influences directly the rate of polymerization ($r \approx kc^{0.8}$) [1]. In certain electrolyte solutions the deposition of polypyrrole fails. A passivation of the electrode during deposition in acetonitrile is sometimes observed and caused by a radical chain polymerization leading to a saturated, nonconductive polypyrrole [2]. The use of basic, aprotic solvents [3,4], the addition of

pyridine [5,6], the application of pyridine-substituted 3-acyl-azopyrroles [7] and of amine-substituted pyrroles [8] impede the polymerization because of a deprotonation of the intermediate radical cation.

Deposition from aqueous solutions with high pH values (NaOH, Na_2CO_3, and $NaHCO_3$ [9]) gives only thin, electro-inactive films or is blocked completely [10,11] which can be explained by the formation of carbonyl groups as a result of nucleophilic attack. The addition of N-methylpyrrole to the electrolyte solution further decreases the conductivity of the films. The addition of organic acid anions with acid constants of $pK_a > 3.4$ causes similar effects [12,13].

In an earlier publication, we have reported a similar observation for the deposition of polypyrrole from aqueous solutions of potassium fluoride [14], where the rate of polymerization decreases rapidly from cycle to cycle during the potentiodynamic electrodeposition. The polypyrrole-fluoride film (PPy|KF) has been detected by cyclic voltammetry, impedance spectroscopy and optical microscopy [14]. Poly(N-methylpyrrole) (PNMPy) however can be prepared easily from these solutions, though its polymerization starts at higher potentials (720 mV versus SCE instead of 650 mV). We had to perform some further experiments and analyse carefully the results in order to achieve a good explanation for this special behaviour during PPy deposition [15].

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2. Experimental details

The electrochemical experiments were performed in a thermostat-controlled (25°C) glass cell with a PVC lid. A platinum-plated Pt electrode was used as counter electrode and a saturated calomel electrode (SCE) as reference electrode. The working electrode (WE) consisted of the circular surface end (area $A_g = 0.2$ cm^2) of a glassy carbon rod, which was stuck into a holder made from PEEK (polyether ether ketone) and contacted at the other end of the rod. Prior to each deposition experiment, the glassy carbon surface was polished with a suspension of Al_2O_3 (1/4 µm particle diameter, Struers). The apparatus for the measurements was a built-in-house system [16], which allowed potentiostatic cell control, cyclic voltammetry, chronoamperometry and impedance spectroscopy. Impedance data could be measured in a frequency range from 10^{-4} to 10^4 s^{-1} at given WE potentials. Either sinusoidal signals were superimposed on the WE potential, followed by current analysis (PARC EG&G, model 5102 lock-in-amplifier, $8-10^4$ s^{-1}) or potential pulses of different length were applied and analysed by fast Fourier transform (FFT, $10^{-4}-8$ s^{-1}).

Salt solutions of 0.1 mol l^{-1} (KF, KCl and mixtures of both salts) were prepared by solving the salts (p.a.) in Millipore water and stored under nitrogen. Pyrrole and N-methylpyrrole were purified by distillation at reduced pressure and also stored under nitrogen. Prior to deposition, the cell was filled with a salt solution containing 0.1 mol l^{-1} pyrrole (or N-methylpyrrole) and purged by nitrogen for 1 h.

The deposition was done by cycling the potential of the WE between a lower potential $E_1 = 0$ V and an upper potential $E_2 = 0.9$ V versus SCE. The scan rate v was usually 50 mV s^{-1}, if not otherwise stated. The charge flow was controlled by parallel numerical integration of the current. At a given total charge, or after a certain number of cycles, the potential was set back to 0 V. Then the solution was exchanged for a monomer-free one, usually of the same electrolyte salt, in some cases of a different one.

For cyclic voltammetry, a PPy|KF film was deposited with a total charge of 0.032 C cm^{-2} ($v = 40$ mV s^{-1}). For characterization, the potential was cycled in a 0.1 mol l^{-1} KF solution between -1.2 and 0.2 V at scan rates of 200 down to 3 mV s^{-1}. At each scan rate, five cycles were recorded in order to allow the dynamic equilibrium to be established.

For impedance analysis, the potential of a PPy|KF film was changed stepwise from 0.1 down to -0.6 V and then increased again to 0.3 V. At each potential, a complete impedance spectrum was recorded, as soon as the residual current after the potential step had attained a constant value beyond 1 µA cm^{-2} caused by irreversible side reactions.

3. Results and discussion

3.1. Self-passivation during electrodeposition

Already the blue colour of the PPy|KF films during electrodeposition shows that the polymer is in its oxidized state.
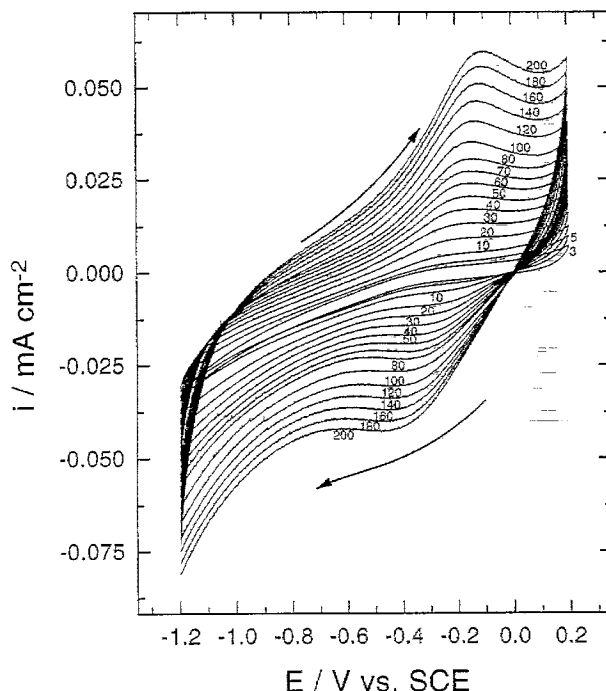

Fig. 1. Cyclic voltammetry of PPy|KF in 0.1 mol l^{-1} KF. The numbers indicate the sweep rate v in mV s^{-1}. Polymer deposited with a total charge of 0.032 C cm^{-2} between 0 and 0.9 V at 40 mV s^{-1}.

In cyclic voltammetry the peaks for the oxidation and the reduction appear clearly (Fig. 1). As reported earlier [14], the charge flux during the potentiodynamic electrodeposition of polypyrrole from an aqueous solution of potassium fluoride (PPy|KF) decreases strongly from cycle to cycle. The polymerization charge in a specific cycle as a function of the total charge flowing during the foregoing deposition is often an exponential decay (Fig. 2), i.e. the electrode is passivated by the polymer deposition.

Already the first cycle of a PPy|KF deposition shows some deviations from the usual behaviour (Fig. 3), as represented by PNMPy|KF: trace crossing which is caused by the nucleation overpotential at the beginning of the polymerization does not occur. An unusual behaviour can also be observed during the potentiodynamic deposition of PPy|KCl if E_2 is
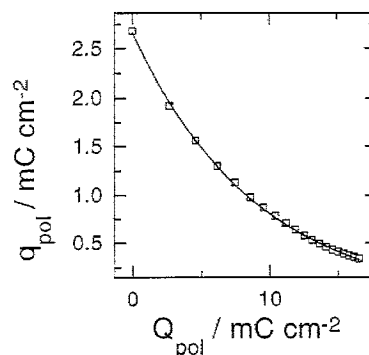

Fig. 2. Exponential decrease of charge flow q_{pol} per cycle. PPy deposition from a 0.1 M NaF solution; the abscissa, total charge $Q_{pol} = \sum_i{}^n q_{pol}$ up to the respective cycle number n is a measure for the thickness of deposited polymer (see Eq. (A1)). Line: exponential fit.
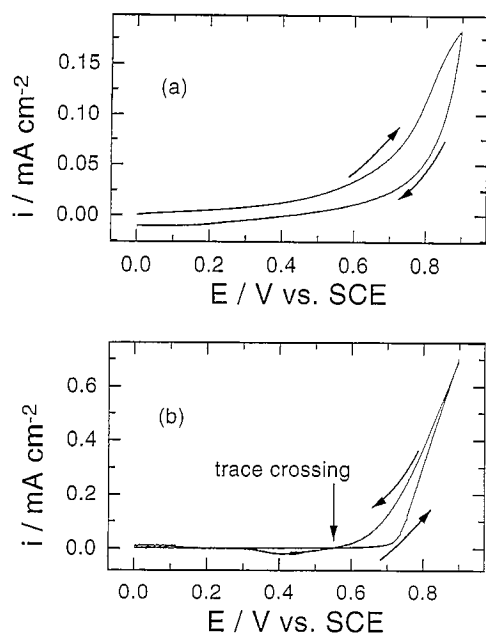
Fig. 3. First cycles during the potentiodynamic electrodeposition of a PPy film (a) and a PNMPy film (b) from aqueous KF solutions. The usual trace crossing (PNMPy) shows the decrease of the nucleation overpotential. For PPy, the currents in the cathodic sweep are always lower than in the first anodic sweep indicating self-passivation.

not larger than 0.7 V [15]. In that case, however, only a few polymer nuclei are formed during the first cycle and the currents are orders of magnitude lower than at the beginning of the PPy|KF deposition, where the currents are even higher than during the deposition from a tosylate electrolyte [15]. So, the lack of trace crossing in the first cycle is not caused by a too low voltage, but by passivation. The relatively high currents at the onset of polymerization also show that the oxidation of a monomer in KF (or NaF) is not more difficult than in other electrolytes.

3.2. Impedance analysis

At first sight, the impedance data of a freshly deposited PPy|KF film in the complex plane show only a single, strongly depressed semicircle at high (1) and a slightly curved line at low frequencies (2) (Fig. 4(a)). Usual interpretation is based on an equivalent circuit of the modified Randles type [16,17] which describes the electrochemistry of many other oxidized polypyrrole layers rather well. The semicircle is attributed to the double-layer capacitance C_{dl} of the polymer|electrolyte interface (at least in the oxidized state) and the charge transfer resistance R_{ct} of the polymer reduction/oxidation reaction. Because of nonidealities (i.e. the interface roughness), a pure double-layer capacitance is not sufficient to describe the situation [16–19], and a constant phase angle element CPE must be used instead ($Z_{CPE} = \sigma(j\omega)^{-\alpha}$, $0 \leq \alpha \leq 1$, often $0.5 \leq \alpha \leq 1$). The intersection of the semicircle with the real axis at high frequencies then gives the sum of the resistances R_E of the electrolyte and of the polymer R_{pol} (140 Ω), the one at low frequencies the
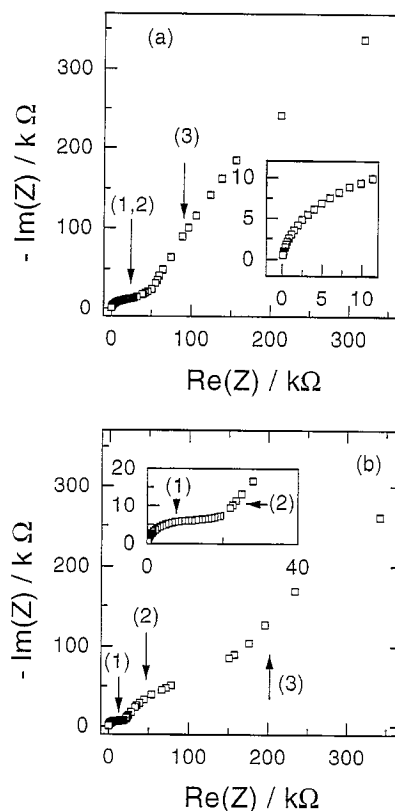

Fig. 4. Impedance spectra of a PPy|KF film at −0.2 V freshly deposited (a) and after reduction and reoxidation (b). After reduction and reoxidation of the fresh polymer, the semicircle (1,2) of (a) splits up in two semicircles (b) overlapping before. They correspond to the bulk properties of the polymer (1) and to the interfacial properties (2). Obviously, the charge transfer resistance of the fresh polymer is lower than that of the older one. At low frequencies (3), mass transport dominates.

sum of those with the charge transfer resistance R_{ct} (40 000 Ω). In the linear region at lower frequencies mass transport limitations in the polymer occur, resulting in a Warburg impedance in the simplest case.

This simple interpretation, however, is inadequate in the case of PPy|KF. When reducing the film and reoxidizing it again, a second semicircle at higher frequencies appears (Fig. 4(b)), which must then be attributed to the properties of the polymer bulk [20] (Fig. 5). This semicircle can scarcely be detected when the polymer is a good electric conductor or when its time constant is too close to that of the semicircle (C_{dl}, R_{ct}). Then, the two semicircles overlap more or less, which happened with the freshly deposited film. The intersections of the bulk semicircle with the real axis give the electrolyte and the polymer resistance. From the diameter and the maximum of the semicircle [18], a polymer capacitance can be estimated [20,21]. Only from this semicircle, can the polymer resistance for the oxidized polymer (7 kΩ) be derived. From the charge used for the synthesis (0.029 C cm^{-2}) and an average density ρ of 1.0 g cm^{-3}, the specific conductivity of PPy|KF could be estimated as 8×10^{-9} S cm^{-1}, a value which is ten orders of magnitude lower than for PPy|KCl films of similar preparation conditions and also
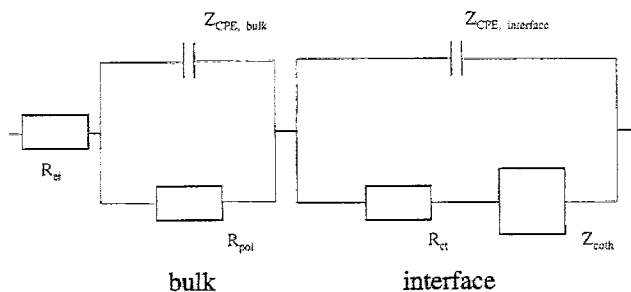
Fig. 5. Equivalent circuit for the analysis of impedance spectra of conducting polypyrroles. Modified Randles circuit, where the interfacial impedance (constant phase element, $Z_{CPE,interface}$, replaces the simple double-layer capacitance C_{dl}, charge transfer resistance R_{ct}, mass transport impedance Z_{coth}, here an expansion of the Warburg impedance Z_W to a finite diffusion element [16,17]) is connected in series with the electrolyte resistance R_{el} and a circuit describing the polymer bulk properties (polymer resistance R_{pol} and constant phase element $Z_{CPE,bulk}$). For large $Z_{CPE,bulk}$, the equivalent circuit simplifies, and the interfacial impedance is connected serially with a resistance $R_{el}' = R_{el} + R_{pol}$.

much lower compared to most PNMPy polymers (around 10^{-3} S cm^{-1} [22]).

The specific conductivity depends on the electrode potential. A complete numerical fit [23] of the spectra with the equivalent circuit of Fig. 5 at different potentials shows that the polymer reduction causes a further decrease in conductivity, as well as high oxidation degrees. These tendencies are generally known for PPy [8,24,25], but at a totally different conductivity level.

3.3. Evaluation of the specific conductivity from synthesis voltammograms

The high resistance of the growing polymer causes a large potential drop across the film and leads to the self-passivation.

In Fig. 6, the anodic half-waves of two typical voltammetric curves of the PPy|KF deposition are shown. Assume that the current depends at a constant sweep rate only on the potential drop at the polymer surface. Then, a current i is measured at a voltage E_A in cycle A and, when more polymer has been deposited and a larger voltage drop is obtained across the polymer, at a higher potential E_B in a later cycle B. From the amount of charge flowing between E_A in A and E_B in B, it is possible to estimate the specific conductivity κ:

$$E_A - E_B = i \frac{\kappa^{-1} M_{PPy}}{2.3 F \rho} (Q_A - Q_B) \qquad (1)$$

A plot of $E_A - E_B$ for a fixed cycle B and different cycles A at constant i versus the differences in polymerization charge yields a straight line through the origin (Fig. 7), and from its slope a value for κ can be calculated. The value for the specific conductivity $\kappa = (6 \pm 3) \times 10^{-9}$ S cm^{-1} agrees with the result of the impedance analysis (see above).

In the derivation of formula (1) (see Appendix A), several approximations are used besides the general neglect of side reactions. So, the specific conductivity is considered to be independent of the potential in the range where the polym-
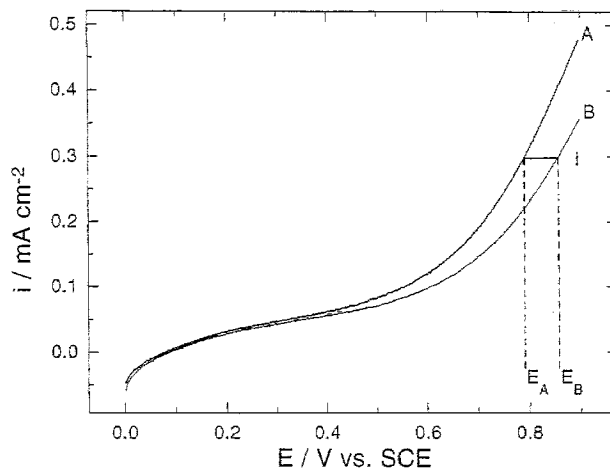

Fig. 6. Shift of the anodic sweep of the synthesis voltammograms due to the increasing polymer resistance. The change in potential of cycle A and a later cycle B at current i from E_A to E_B can be attributed to an ohmic potential drop across the freshly deposited polypyrrole, $E_B - E_A = R_{pol} i$.
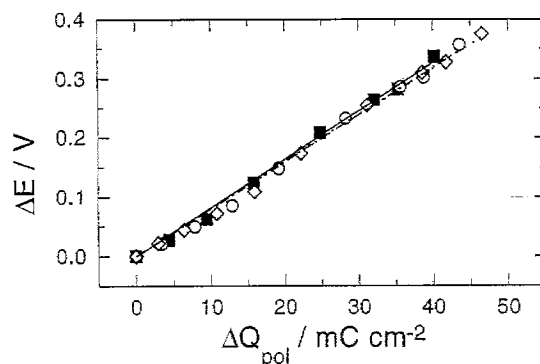

Fig. 7. Specific conductance of PPy|KF from the synthesis voltammograms. The potential differences $E_B - E_A$ (see Fig. 6) are plotted for three different currents i at 900 mV of three different cycles B (■, No. 26; ○, No. 31; ◇, No. 36) vs. the change in polymerization charges, which are proportional to the freshly deposited amount of polymer.

erization takes place, and to be the same everywhere in the whole polymer. As nucleation causes an additional overpotential, neither the first cycle could be taken for the analysis, nor cycles from the end of polymer deposition, because the precision of i decreases compared with the capacitive background currents.

3.4. Exchange experiments

If one exchanges the pyrrole/KF solution from which the polymer was deposited for a pyrrole/KCl solution, the deposition of PPy|KCl occurs in nearly the same way as on a fresh glassy carbon electrode. Obviously, the exchange of fluoride for chloride is rapid. In KCl solutions, cyclovoltammograms of PPy prepared in KF solution look similar to those prepared in KCl solution [15]. The substitution of fluoride obviously increases the conductivity of the polymer layer to values usual for PPy|KCl. Therefore, it must be concluded that a direct interaction of the fluoride ions with the positive charge carriers in the polymer blocks the charge transport.

This interpretation is supported by a series of experiments, where polypyrrole was deposited from mixed solutions of KF and KCl with a constant ion strength of 0.1 mol l^{-1}. Even a small amount of fluoride slows down the polymer formation significantly, and a high excess of chloride is necessary to achieve a behaviour similar to that in pure KCl solution (Fig. 8). Even in the case of a four-fold excess of KCl, the first voltammetric cycle shows no trace crossing and the charge increases only by 2 mC cm^{-2} (Fig. 8(a)) compared to the preparation from a pure KF solution, and to the charge increase (6 mC cm^{-2}) in pure KCl solution. Probably at the beginning of the deposition only PPy|KF is formed. In the first cycles (a) processes are observable leading to a non-exponential curve, sometimes even for pure KF. The polymer nucleation is probably strongly affected by the presence of fluoride. The amount of fluoride incorporated during the nucleation on the substrate from mixed solutions is not necessarily identical to that during further polymer growth. Selectivity of PPy films for different anions is known from the literature [26]. Generally, it must be assumed that the fluoride content in the polymer is larger than in the solution. That is why even in a solution of 30% KF, it needs more than 70 cycles to deposit a charge of 300 mC cm^{-2} (corresponding to 1 μm film thickness), whereas in pure KCl only 14 cycles are necessary. The interplay between nucleation and growth processes causes, in the solutions from 0 to 70% KCl, an intermediate increase in the polymerization rate after the first cycles. Finally, the polymerization rate decreases because the increasing polymer thickness leads to a higher resistance. The less KF in the solution, the later the final decrease of the polymerization rate occurs.

Impedance spectroscopy could be performed without exchange of the electrolyte because, in the range of applied potentials, no further polymerization occurs. The influence of the fluoride content is best visible in the Bode plots (Fig. 9, at 0 V versus SCE).

For frequencies larger than 1000 s^{-1}, the magnitude of the impedance is nearly frequency-independent for pure PPy|KCl films and the phase angle is very low there (range 1). When lowering the frequency, the magnitude of the impedance increases and the phase angle passes through an extremum. In this region, which corresponds to the largest part of the semicircle discussed in the framework of the Randles circuit (Fig. 5), the charge transfer resistance and the double-layer capacitance (or the corresponding CPE) determine the shape of the spectrum (range 2). At low frequencies, mass transport phenomena and adsorption processes dominate the impedance behaviour (range 3).

Two important things can be seen now in range 1 for increasing fluoride content of the solution:

(1) The magnitude of the impedance increases and becomes frequency-dependent for more than 20% KF.

(2) The phase angle at high frequencies increases. Obviously a similar feature to that in range 2 appears. A tendency to develop an extremum above the measured frequencies can be seen, which comes closer and closer with increasing KF content. In pure KF, it has reached almost 10^4 s^{-1}.

This behaviour corresponds to the appearance of a second semicircle in Fig. 4(b) and demonstrates once again the increase in the polymer resistance with KF content.

3.5. Discussion of the polymer resistance

The number of charge carriers should be sufficient to achieve a good conductivity. Therefore it must be assumed that the mobility of the charge carriers is the limiting factor for the conductivity.

Which mechanism is responsible for the immobilization of the charge carriers? The fluoride ion could interact electrostatically with the positive charges in the polymer backbone and pin them. This however is not very probable, because such an effect is not observed during polymerization of N-methylpyrrole. So, it must be concluded that the fluoride ion interacts with hydrogen of the pyrrole nitrogen, leading to a localization of the positive charge of the polymer on the hydrogen atoms (Fig. 10). It is now no longer available for electronic charge transport, so that the polymer is in an oxidized, but nearly nonconducting state. This situation is similar to the expulsion of protons as an alternative charge compensation mechanism during polymer oxidation [27]. Here, however, the hydrogen is not split off. In chloride solutions, an ion exchange occurs, and the positive charge is delocalized and takes over its electronic role in the conjugated polymer. Therefore, special growth processes of the polymer backbone in the presence of F^- seem to be absent.
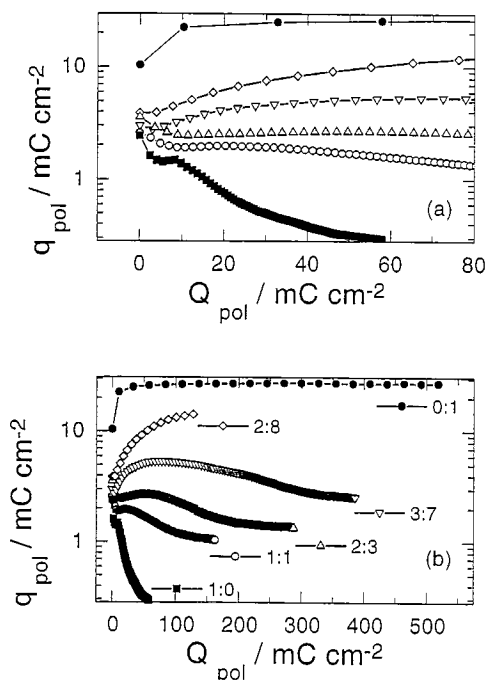

Fig. 8. PPy deposition from KF/KCl mixed electrolytes of different composition. Polymerization charge per cycle q_{pol} vs. total charge Q_{pol}. Ionic strength: 0.1 mol l^{-1}. Numbers indicate the ratio of the two salts: (a) first synthesis cycles; (b) all cycles.
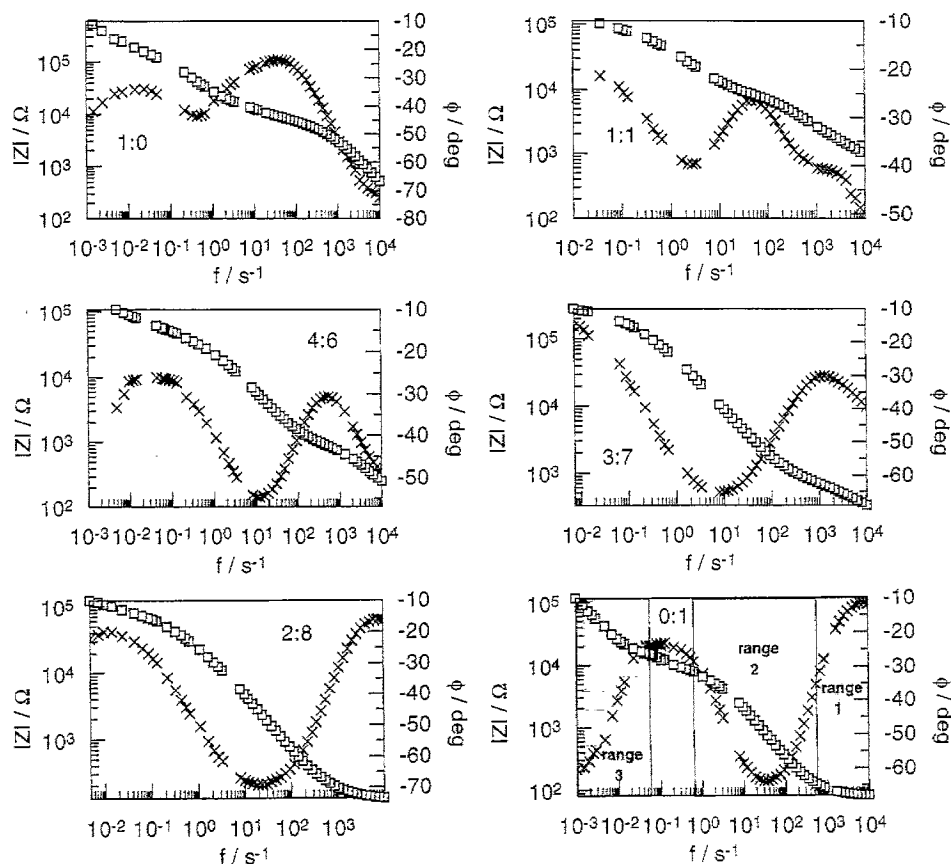
Fig. 9. Impedance data of polypyrrole films deposited and investigated in mixed solutions of KCl and KF. The number indicates the relation from KF to KCl (ionic strength: 0.1 mol l⁻¹): ×, phase angle; □, magnitude of the impedance. Potential: 0.0 V vs. SCE.
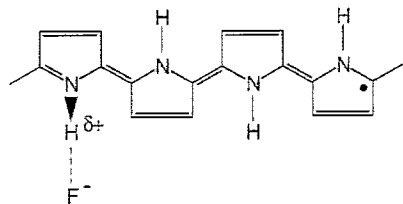

Fig. 10. Model of the F⁻ interaction in PPy|KF. By interaction of a polaron (radical cation) with the fluoride ion the positive charge is localized and no longer available for electronic conduction.

4. Conclusions

The interaction of fluoride anions with the hydrogen atoms at the pyrrole nitrogen of polypyrrole leads to a localization of the positive charge on the hydrogen. So the polymer is almost nonconductive, in contrast to the PNMPy system where the methyl group prevents this effect.

The order of magnitude of the resistance is evaluated as well by impedance spectroscopy as directly from the synthesis voltammograms.

Ion exchange experiments permit us to exclude irreversible defects in PPy, like crosslinking or carbonyl group formation in the polymer backbone, as the main reason for the high resistance.

Already minor amounts of KF in KCl solutions prevent the trace crossing in the first cycle and slow down further growth.

This shows that fluoride ion incorporation in the polymer is favoured.

Appendix A

Derivation of formula (1)

At a given time during the polymerization, the polymer resistance R (normalized to the geometric area A_g of the electrode) is proportional to the total amount of charge Q flowing until this time (assuming a transfer of 2.3 electrons per pyrrole unit during polymerization):

$$R = Q \frac{\kappa^{-1} M_{PPy}}{n_e F \rho} \tag{A1}$$

where M_{PPy} is molar weight of PPy|KF, ρ polymer density,

F Faraday constant, $n_e = 2.3$ (electrons per PPy unit), and κ specific conductivity (constant).

Neglecting nucleation effects and a change in the surface area of the polymer, the current in cycle n at a potential E depends only on the potential drop E_{real} at the electrode. So one can write for the anodic half-sweep:

$$i(n,E) = f(E_{real}) = f[E - iR(n,E)] \qquad (A2)$$

Within the potential ranges of synthesis, the current rises monotonically with the potential. So the (unknown) function f in Eq. (A2) is injective and the reversed function can be applied. Then, the substitution of $R(n,E)$ by Eq. (A1) yields:

$$f^{-1}(i) = E - i(n,E) \; Q(n,E) \; \frac{\kappa^{-1} M_{PPy}}{2.3 F \rho} \qquad (A3)$$

With a scan rate v, $Q(n,E)$ in Eq. (A3) is just the result of the integration of the current:

$$v Q(n,E) = \left[\sum_{k=1}^{n-1} \oint i(E',k) \; dE' \right] + \int_{E_u}^{E} i(E',n) \; dE' \qquad (A4)$$

Even if the function f were known, Eq. (A3) could not be solved analytically for $i(n,E)$ by substituting Q for Eq. (A4). However, $Q(n,E)$ is easily determined by numerical integration of the voltammogramms. Then, one can apply Eq. (A3) to the same current i in two different anodic half-cycles A and B. This current will flow at two different potentials E_A and E_B, respectively. Thus, one writes Eq. (A3) for A and B and calculates the difference:

$$0 = E_A - E_B - i \; \frac{\kappa^{-1} M_{PPy}}{2.3 F \rho} \; [Q(A,E_A) - Q(B,E_B)] \qquad (A5)$$

Eq. (A5) is equivalent to Eq. (1).

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