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Electrochemical measurements of the ion conductivity, permselectivity and transference numbers of polypyrrole and polypyrrole derivatives

Abstract Electrochemical dc and ac measurements were carried out on free-standing polypyrrole (ppy) membranes to study the ion conductivity and permselectivity of the polymer as a function of the oxidation state. The membranes were prepared by electropolymerisation and mounted in a two-compartment cell, where the oxidation state of the ppy membrane could be adjusted by potentiostatic polarisation and the ion conductivity and permselectivity of the polymer could be measured in a symmetrical electrolyte/membrane/electrolyte configuration. Combining constant current permeation experiments with solution analysis using ion chromatography (IC) and atomic absorption spectroscopy (AAS), it was demonstrated that ppy exhibits not only an appreciable ion conductivity but also a distinct permeability and selectivity for anions in the oxidised state. Incorporation of immobile anions like dodecylsulfate or copolymerization with a modified pyrrole monomer like *N*-sulfopropyl-pyrrole carrying a sulfonate group leads to modified membranes which exhibit distinct cation permselectivity in the reduced state. Such a membrane can be switched dynamically between anion and cation permeability through electrochemical oxidation and reduction of the polymer backbone.

Key words Conducting polymers · Polypyrrole · Membranes · Ion conductivity

Introduction

Conducting polymers are interesting organic materials which offer a large variety of potential applications, e.g.

in the field of battery technology and energy storage, corrosion protection, electromagnetic shielding, anti-electrostatic coatings, electrochromic or mechanical devices (displays, artificial muscles), or modified electrodes for chemical and biochemical sensors [1–18].

Many properties of the intrinsically conducting polymers (ICPs) are strongly related to their oxidation state, which is easily controlled by electrochemical oxidation/reduction processes. From the view point of electrochemistry one of the most interesting aspects is the coupling between electron charge transfer and the exchange of counterions during the process of doping/undoping the polymer. The majority of these studies were done on modified electrodes, i.e. metal/polymer/electrolyte (asymmetric systems). The first measurements on free-standing membranes, i.e. electrolyte/polymer/electrolyte (symmetric systems), were carried out by Burgmayer and Murray [18–20] on polypyrrole. They could demonstrate that the ion conductivity of the membrane can be changed by polarisation at different potentials. A great deal of work is directed towards the preparation of a number of polypyrrole derivatives with modified electrical, electrochemical and catalytic properties [21–28]. Other studies deal with the investigation and characterisation of electrochemical redox processes including the exchange of anions and cations with the electrolyte solution [29–37].

Recently, electrochemical impedance measurements have gained increasing interest for the study of the dynamic processes of electron charge transfer and ion transport [38–48]. Using symmetrical and asymmetrical configurations new information on the charge transfer of electrons and ions at the phase boundaries, the conduction mechanisms and the coupling of electron and ion in the bulk polymer can be obtained [49–52].

Information on the permselectivity of conducting polymers is scarce and transference numbers of certain anions or cations are not available in the literature. Therefore, our investigations were directed towards a study of the ion conductivity and permselectivity of polypyrrole and its derivatives under defined dc polari-

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sation conditions. For this purpose a specially designed free standing membrane was developed, which on the one hand makes it possible to adjust the oxidation state of the polymer to a predetermined value and on the other hand allows the measurement of the ion-conducting properties [53–56]. These studies were also directed towards distinguishing the polymer permselectivity for anions and cations and, furthermore, to modify the composition of the polymer membrane by incorporation and copolymerisation of immobile anions during the electropolymerisation process.

Experimental

Figure 1 shows the experimental set-up and a sketch of the membrane construction. The membranes were prepared by electropolymerisation from aqueous solutions onto a microporous polycarbonate foil of 30 μm thickness. The size and the number of the pores were generated by ion spurs etching with NaOH. The substrate is characterised by a pore density of $N_p = 1.5 \times 10^7 \, cm^{-2}$ and a pore radius of $r_p = 0.8 \, \mu m$. This corresponds to a porosity of 0.3. The polycarbonate foil was covered with a thin sputtered gold film of 70 nm thickness as electronic support. The membrane was fixed in a PTFE frame and mounted in a symmetrical two-compartment cell. Electrical contact was made by a thin gold wire so that the polypyrrole could be electrodeposited on one side of the supporting membrane. The pores of the foil were completely covered by the homogeneous polymer film. The geometrical area of the polymer membrane in contact with the electrolyte was 0.78 cm². The thickness of the polymer layer varied between 7.5 and 20 μm and was estimated from the anodic charge consumed during the polymerisation process ($240 \, mC \equiv 1 \, \mu m \, cm^{-2}$) [1, 2].
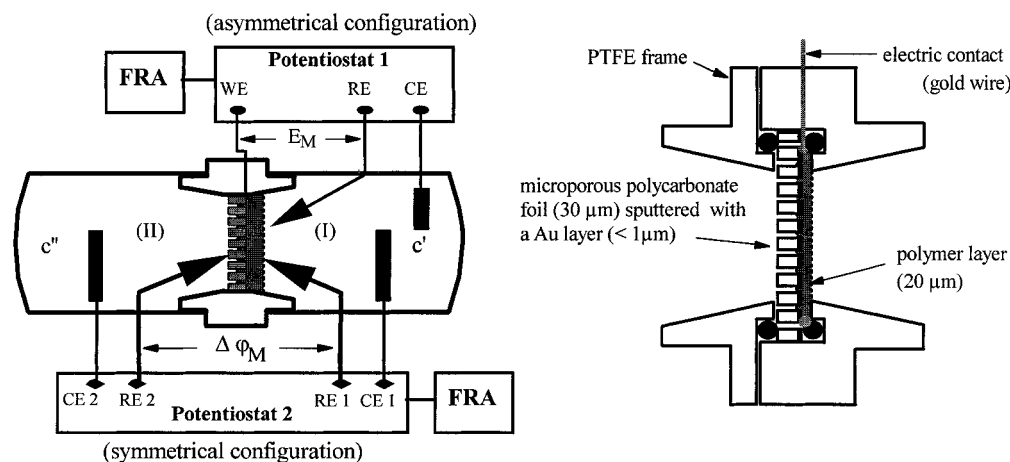
The three different types of membranes studied were prepared from the following solutions:

Polypyrrole (ppy): 0.1 M pyrrole + 0.1 M KCl
Dodecylsulfate-modified polypyrrole (ppy/dcs): 0.1 M pyrrole + 0.1 M Na-dodecylsulfate
Copolymer polypyrrole/n-sulfopropyl-pyrrole (ppy-nspy): 0.1 M pyrrole + 0.1 M KCl + 3.7×10^{-4} M n-sulfopropyl-pyrrole

As the standard procedure, electropolymerisation was performed under potentiodynamic cycling between 600 mV and 650 mV vs an Ag/AgCl, KCl(sat.) reference electrode at a constant sweep rate of $|dE/dt| = 20 \, mV \, s^{-1}$. This gave much smoother films than polymerisation at constant potential or constant current. During the electropolymerisation, the electrolyte was pumped continuously through the cell. To obtain the optimum performance of the copolymer membrane with respect to ion conductivity and anion/cation switching, polymerisation experiments were carried out with different ratios of the pyrrole/n-sulfopropyl-pyrrole concentrations as proposed by Doblhofer et al. [35]. The membranes were characterised and tested for tightness by impedance and membrane potential measurements. It was found by SEM that the polymer film is grown on top of the polycarbonate substrate without deeply penetrating the pores.

The experimental set-up of the electrochemical measurements is also shown in Fig. 1. In the asymmetrical configuration, the oxidation state of the membrane can be adjusted by potentiostatic prepolarization at a defined potential E_M. In the symmetrical configuration, the ionic current through the membrane can be measured as a function of the potential difference $\Delta\varphi_M$ across the membrane. Additionally, impedance measurements which are not reported here could be carried out in both configurations using the frequency response analyser FRA.

Results and discussion

Direct evidence for ion conductivity and permselectivity of electronic conducting polymers can be obtained from different types of dc polarisation experiments and Donnan potential measurements on free-standing membranes. This has been demonstrated previously for pure polypyrrole (ppy) and dodecylsulfate-modified polypyrrole (ppy/dcs) [53–56]. In recent experiments on the copolymer polypyrrole/n-sulfopropyl-pyrrole (ppy-nspy), it could be shown that a membrane can be designed which exhibits both anion and cation exchanger properties, depending on the oxidation state [56].

Ion conductivity of ppy and dodecylsulfate-modified ppy/dcs membranes

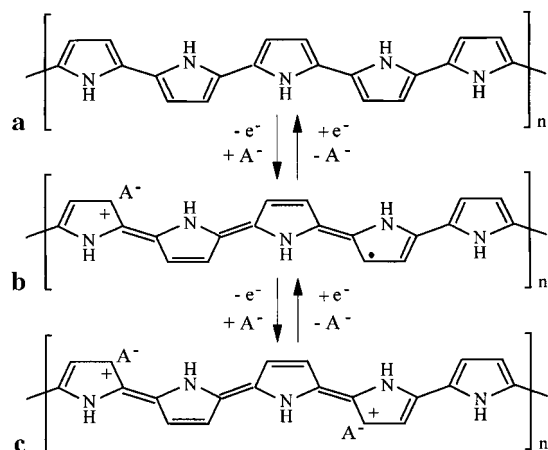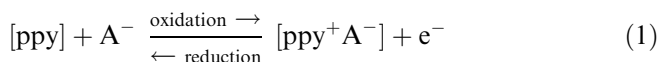For pure polypyrrole, it is generally accepted that the oxidation/reduction of the polymer

Fig. 1 Experimental set-up for the electrochemical measurements on free standing membranes using three-electrode technique (asymmetrical configuration) and four-electrode technique (symmetrical configuration) and details of the membrane construction

Fig. 2a–c Limiting structures of polypyrrole during oxidation and reduction

Fig. 3 Current density i vs the membrane potential difference $\Delta\varphi_M$ after prepolarisation at different potentials E_M; system: 01 M KCl/ppy/01 M KCl

$$[\text{ppy}] + A^- \xrightarrow[\longleftarrow \text{ reduction}]{\text{oxidation } \longrightarrow} [\text{ppy}^+ A^-] + e^- \qquad (1)$$

connected with an exchange of charge-compensating anions A^- between the polymer and the electrolyte.

Figure 2 shows three limiting structures of the polymer chain in the reduced and oxidised state of polypyrrole. From quartz crystal microbalance measurements it was found that also cations can be exchanged at a low degree of oxidation because of the immobility of a certain amount of anions in the polymer [30, 37].

In the particular case of the modified ppy/dcs film electrode, the counterion dodecylsulfate, which is incorporated during the electropolymerisation process, cannot be exchanged because of its long-chain structure and low mobility in the film. Therefore, cations will preferentially enter the film during the reduction of the polymer to compensate the negative charge of the remaining dodecylsulfate anions.

$$[\text{ppy/dcs}^- K^+] \xrightarrow[\longleftarrow \text{ reduction}]{\text{oxidation } \longrightarrow} [\text{ppy}^+/\text{dcs}^-] + K^+ + e^- \qquad (2)$$
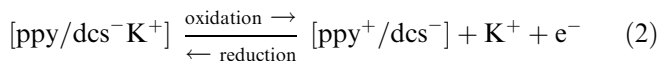
This is also evident from characteristic changes in the shape of the cyclic voltammogram of these polymer film electrodes, indicating energetically different situations with respect to counterion exchange and conformational changes in the system [56]. Information on the relative contribution of anion and cation exchange processes has also been obtained from quartz crystal microbalance measurements [28, 30, 37].

The fact that anions or cations are exchanged between the electrolyte solution and the polymer during electrochemical oxidation/reduction suggests that conducting polymers should also exhibit a distinct ion conductivity. In the case of pure polypyrrole (ppy), anion conductivity is expected in the oxidised state, whereas cation conductivity is expected to appear in the reduced state of the modified polypyrrole (ppy/dcs).

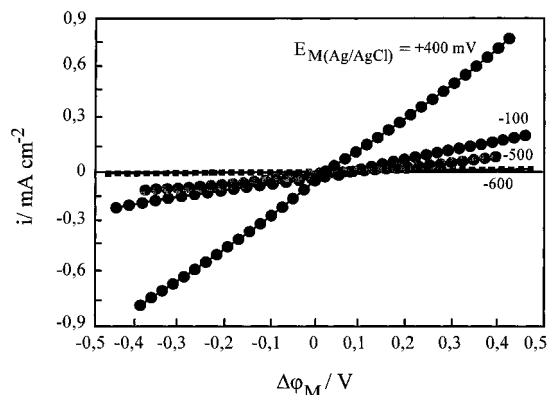To determine the ion conductivity and to distinguish between preferred anion and cation transport properties (permselectivity), measurements were carried out on a free-standing membrane. Under these conditions, the polymer is in contact with the electrolyte on both sides and the electron transfer is completely blocked. The ionic dc conductivity can thus be determined by measuring the ionic current through the membrane as a function of the potential drop $\Delta\varphi_M$ across the membrane (see symmetric configuration in Fig. 1).

Figure 3 shows the dependence of the dc current density i through a polypyrrole membrane as a function of $\Delta\varphi_M$ at different oxidation states. In this experiment, the oxidation state was adjusted by prepolarization of the polymer film at constant potentials E_M for about 10 min (see asymmetric configuration in Fig. 1). Independently of the prepolarization potential E_M, the i vs $\Delta\varphi_M$ curves in Fig. 3 exhibit purely ohmic behaviour

$$i = \varepsilon \frac{\sigma}{d} \Delta\varphi_M \qquad (3)$$

where σ is the ion conductivity, d the thickness of the membrane and ε a factor which takes into account the non-cylindrical current distribution in the film. Assuming in a first approximation a conical geometry of the current flux in front of the pores, ε can be calculated from simple geometrical relations [56].

From the given parameters r_p and N_p of the system and the value of the radius $r_d = 1.5 \times 10^{-4}$, which was obtained from N_p^{-1}, a geometrical factor of $\varepsilon = 0.57$ was calculated. Since the film thickness d and the geometrical factor ε are known quantities, the ion conductivity σ can be calculated from the slope of the i vs $\Delta\varphi_M$ curves according to Eq. 3.

From Fig. 3 it is evident that the ion conductivity decreases significantly with decreasing potential E_M. At the most positive potential $E_M = 400$ mV, the ppy membrane is in the oxidised state, where the number of defects in the π-electron system is at its maximum. At $E_M = -600$ mV, the membrane is almost completely reduced and the π-electron system is fully occupied. For polypyrrole it was found that σ increases exponentially with the applied potential E_M. This is shown by the
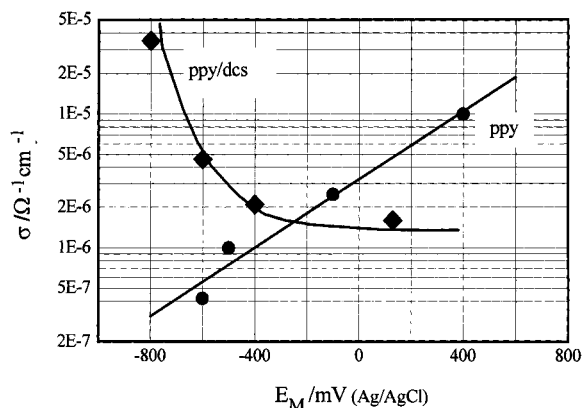
Fig. 4 Ion conductivity σ as a function of the prepolarisation potential E_M for a ppy membrane and the dodecylsulfate modified ppy/dcs membrane obtained from dc measurement in the system 01 M KCl/membrane/01 M KCl

linear dependence of log σ vs E_M in Fig. 4, which can be expressed in terms of the following relation:

$$\log \sigma = \log \sigma_{max} + \beta\left(E_M - E_{M,max}\right) \qquad (4)$$

where σ_{max} denotes the value of σ at the prepolarisation potential $E_{M,max} = +0.4$ V. The proportionality factor β was found to be

$$\beta = \frac{d \log \sigma}{d E_M} = 1.4 \text{ V}^{-1} \qquad (5)$$

Similar experiments were also carried out using a membrane of the modified ppy/dcs polymer film. The results are also shown in Fig. 4. In this case, the ion conductivity σ is at its maximum in the reduced state and decreases significantly with increasing potential E_M. However, the dependence of σ on E_M does not exhibit exponential behaviour. The main decrease of σ takes place in a narrow potential range between -800 mV and -400 mV, where the polymer is in the reduced state.

Permeability of ppy and dodecylsulfate modified ppy/dcs membranes

Permeation experiments at constant current (1 mA cm^{-2} $\leq i \leq$ 4 mA cm^{-2}) through the membrane were carried out for a quantitative analysis of the permselectivity. The permselectivity is experimentally available by analysing the electrolyte solutions on both sides of the membrane with respect to the permeating ion. Figure 5 shows the corresponding experimental conditions with Na$_2$SO$_4$ in the anodic and KCl in the cathodic cell compartment.

The concentrations of Cl$^-$ and Na$^+$ were analysed in both compartments using ion chromatography (IC) and atomic absorption spectro-scopy (AAS) respectively. In the case of the oxidised polypyrrole (Fig. 5), the Cl$^-$ concentration in compartment (I) was found to increase linearly with time, while the Na$^+$ concentration in compartment (II) remained almost at zero level.
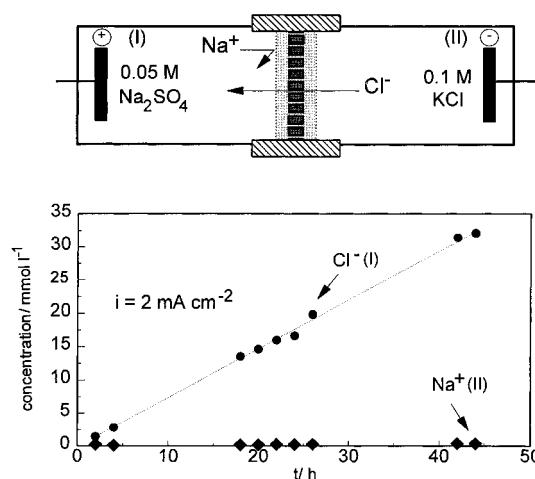

Fig. 5 Permeation experiment at constant $i = 2$ mA cm^{-2} with a ppy membrane in the oxidised state; system composition is given at the *top* of the figure

The dynamic transference number of Cl$^-$ in the membrane can be obtained from the concentration time dependence in Fig. 5 according to the following relation

$$t^M_{Cl^-} = \frac{d c_{Cl^-}}{dt} \frac{z_i F V_c}{i A_g} \qquad (6)$$

where $V_c = 100$ dm^3 is the electrolyte volume of the anodic cell compartment. A transference number of $t^M_{Cl^-} = 0.977$ was found from the experiments, indicating a high anion permselectivity of the membrane. The corresponding experiment using the modified ppy/dcs membrane in the reduced state is shown in Fig. 6. In this case, the concentration of Na$^+$ in the cathode compartment is found to increase linearly with time, whereas the Cl$^-$ concentration in the anode compartment remains unchanged at a low level. This indicates cation permeability of the modified ppy/dcs membrane in the reduced
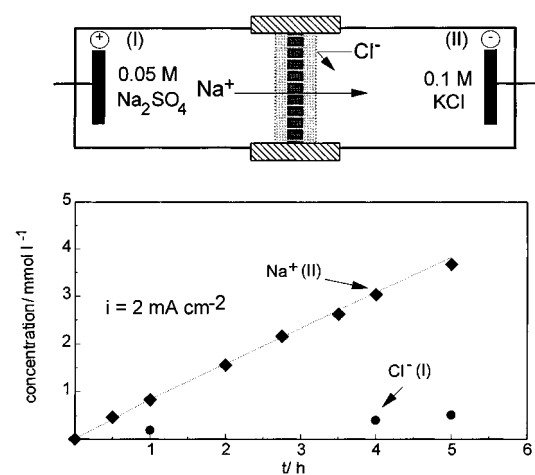

Fig. 6 Permeation experiment at constant $i = 2$ mA cm^{-2} with a ppy/dcs membrane in the reduced state; system composition is given at the top of the figure

state. The dynamic transference number of Na$^+$ was found to be $t_{Na^+}^M = 0.89$.

Corresponding experiments with LiClO$_4$ instead of KCl gave a transference number of $t_{Li^+}^M = 0.9$ and a dc conductivity of $\sigma = 7.83 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$.

The superior permselectivities of ppy and ppy/dcs could also be confirmed by Donnan potential measurements ($i = 0$). In this case the membrane potential φ_M across the membrane:

$$\varphi_M = \frac{RT}{z_i F}(t_i^M - t_{co}^M)2.303 \log\frac{c_i'}{c_i''} = B \log\frac{c_i'}{c_i''} \quad (7)$$

was measured as a function of the concentration ratio c'/c'' of the system:

$$c'' = 0.1\ M\ KCl/membrane/c' = x\ M\ KCl$$
$$(10^{-4} \leq x \leq 10^{-1}).$$

In Eq. 7 the index i denotes Cl$^-$ or K$^+$ and t_{co}^M the transference number of the co-ion.

Figure 7 shows the dependence of φ_M on the concentration ratio $\log(c'/c'')$ for the oxidised ppy and the reduced ppy/dcs membranes. In both cases the membrane potential follows a linear dependence on the logarithm of the concentration ratio with a slope B close to ± 59 mV, where the sign depends on the charge z_i of the permeable ion Cl$^-$ or K$^+$.

The static transference numbers t_i^M were obtained from the slope B of the experimental curves in Fig. 7.

Taking into account that $t_i^M + t_{co}^M = 1$, Eq. 7 leads to

$$t_i^M = \frac{1}{2.303}\frac{z_i F}{RT}\frac{B}{2} + \frac{1}{2} \quad (8)$$

From these experiments the following values of the static transference numbers were derived:

$t_{Cl^-}^M = 0.92$ (ppy membrane in the oxidised state)

$t_{K^+}^M = 0.88$ (ppy/dcs membrane in the reduced state)

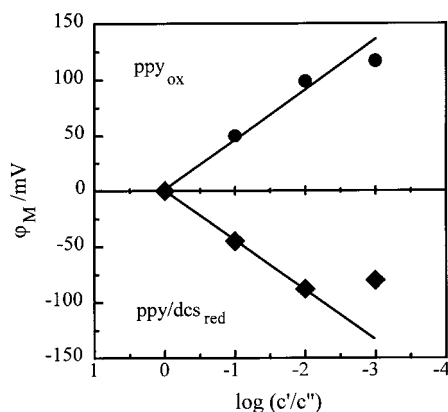These numbers are in good agreement with the values of the corresponding dynamic transference numbers discussed above.

Fig. 7 Dependence of the Donnan-potential φ_M on the concentration ratio c'/c'' in the system $c'' = 01\ M\ KCl/membrane/c' = x\ M\ KCl$ ($10^{-4} \leq x \leq 10^{-1}$) for an oxidised ppy and reduced ppy/dcs membrane

Switchable anion/cation permeability of the copolymer ppy-nspy membrane

A membrane which combines both anion and cation permselectivity was prepared by incorporating a certain number of fixed anionic charges into the polymer chain. This was achieved by electrochemical copolymerisation from a solution containing a mixture of the pyrrole and the chemically modified n-sulfopropyl-pyrrole (nspy$^-$) monomer, schematically shown in Fig. 8.

The copolymer is characterised by the substitution of the proton at the nitrogen atom in the pyrrole ring for the anionic propylsulfonate group C$_3$H$_6$–SO$_3^-$. Depending on the relative concentration of the positive charges ppy$^+$ and the negative charges nspy$^-$, an anion or cation permselectivity was predicted [35]. Since the concentration of ppy$^+$ can be changed electrochemically by oxidation or reduction, both states are related to the condition:
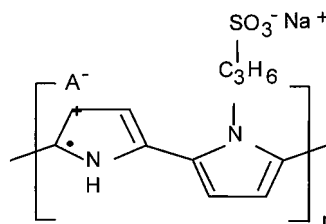
$$[ppy^+] \ll [nspy^-] \xrightleftharpoons[\leftarrow \text{reduction}]{\text{oxidation} \rightarrow} [ppy^+] \gg [nspy^-]$$
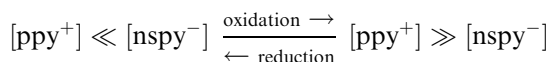
Cation conductivity,	Anionic conductivity,
low electronic conductivity	high electronic conductivity

Permeation experiments in the oxidised and reduced state were carried out in the systems

System I 0.05 M Na$_2$SO$_4$/ppy-nspy/0.1 M KCl
System II 0.1 M LiClO$_4$/ppy-nspy/0.1 M KCl

at constant current density combined with solution analysis for the corresponding ions in the anode and cathode compartments of the cell. As shown in Fig. 9, the oxidised membrane is preferentially permeable to Cl$^-$, whereas in the reduced state the main charge carriers are the cations Na$^+$ or Li$^+$ in systems I and II respectively. Switching from the oxidised to the reduced state, such a membrane changes from anion to cation permselectivity. The switching period is in the order of 20 min. The ion conductivity σ of this membrane as a function of the prepolarisation potential E_M obtained from dc measurements in 0.1 M KCl solution is shown in Fig. 10 together with the conductivity data of the pure ppy and the ppy/dcs membranes. In accordance with the permeation experiments, the conductivity increases at

nspy = n-sulfopropyl-pyrrol

Fig. 8 The copolymer ppy$^+$-nspy$^-$

Fig. 9 Permeation experiments at constant current density $i = 2$ mA cm^{-2} in systems I and II with oxidised and reduced copolymer ppy-nspy membrane
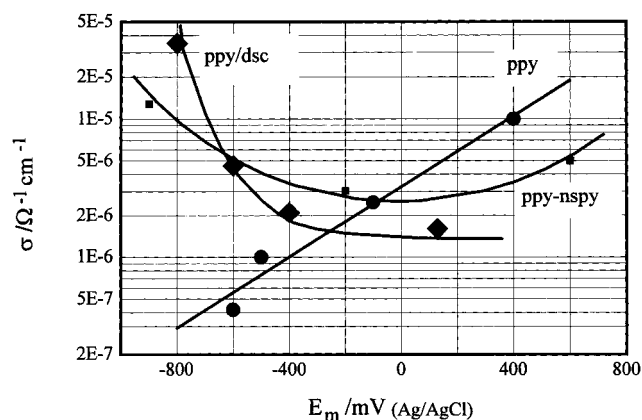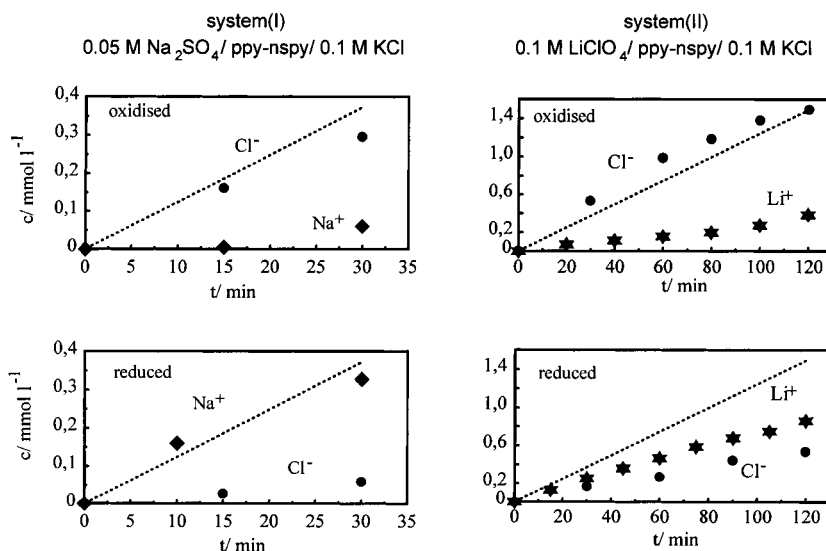
system(I)
0.05 M Na$_2$SO$_4$/ ppy-nspy/ 0.1 M KCl

system(II)
0.1 M LiClO$_4$/ ppy-nspy/ 0.1 M KCl

Fig. 10 Ion conductivity σ as a function of the prepolarisation potential E_M for the ppy membrane and the modified ppy/dcs and ppy-nspy membranes obtained from dc measurements in 01 M KCl

vouring the conduction of mobile counterions in the polymer. High permselectivity for anions was confirmed experimentally for polypyrrole in the oxidised state. Incorporation of long chain anions with low mobility in the polymer leads to pronounced cation permeability in the reduced state. A membrane combining both anion and cation conductivity in the oxidised and reduced state respectively can be prepared by copolymerisation of the monomers pyrrole and the modified n-sulfopropyl-pyrrole carrying a sulfonate group. Such a system can be switched electrochemically between anion and cation permeability and behaves like an anion or cation exchanger membrane.

positive potentials, where the membrane is in the oxidised state and the concentration of mobile Cl$^-$ ions is high, but σ also increases at negative potentials, where the membrane is in the reduced state and K$^+$ ions enter the polymer as mobile counterions for charge compensation of the fixed SO$_3^-$ groups. The overall dc conductivity is about one order of magnitude lower than that of the ppy and ppy/dcs membranes.

Conclusions

Polypyrrole is one of the most famous conducting polymers, exhibiting not only electronic but also remarkable ion conductivity. Similar to the dependence of the electronic conductivity on the doping level, the ion conductivity is found to be strongly dependent on the oxidation state of the polymer. Obviously the defects in the π-electron system act as positive charge centres fa-

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