

Short communication

A voltammetry study on the diffusion of counter ions in polypyrrole films

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Abstract

Polypyrrole (PPy) films doped with large immobile dodecyl benzene sulfonate (DBS) anions have been cycled in electrolytes of different concentration in an investigation of the diffusion of counter ions in this polymer complex. The diffusion of counter ions determines the speed of response of the films when they are used in artificial muscles or as electrodes in batteries and other devices. For the present study, PPy/DBS films were electro-polymerized on platinum wires and cycled in aqueous solutions of NaCl of concentrations ranging from 0.1 M to 5 M. Significant changes in the redox properties of the films were observed with the increase of the concentration. The effective diffusion coefficients in 0.1 M, 1 M and 3 M NaCl are nearly $3 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$, $20 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ and $55 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$, respectively. The diffusion coefficient in 3 M NaCl is approximately 18 times the value in 0.1 M NaCl reflecting that the amount of salt and solvent taken up by the polymer is linked to the electrolyte composition by osmotic balances. These findings have implications for the design of polypyrrole based electrodes and actuators that are required to operate at higher frequencies.

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1. Introduction

Electronically conducting polymers are of interest to solid-state ionics because their properties are determined by the presence and movement of ions. Most of these polymers are insulators intrinsically and become conducting only when doped with counter ions. These polymers have many interesting and unique physical, chemical and optical properties [1]. Since the ion transport in most conducting polymer films is much slower than the electron transport, ion transport governs their redox properties [2]. Among the conducting polymers, polypyrrole (PPy) and its derivatives have attracted considerable attention because of their stability and potential use in actuators, sensors, batteries and capacitors.

When PPy films are cycled in appropriate electrolytes, the reversible redox switching of the film is accompanied by diffusion of counter ions into the polymer matrix to maintain charge neutrality. The dominant mobile species during the doping/undoping of the polymer can vary depending on the particular polymer-ion-solvent interactions. In general, the ion

transport mechanism is not straight forward, since ion pairs and solvent molecules can also participate in this process, resulting in complex electrochemical behaviour [3]. For this reason the kind of counter ions and its concentrations in the supporting electrolyte, solvents and the structure of the polymer have much influence on the doping mechanism. The supporting electrolyte/solvent systems used showed a large effect on both electro-activity and long term charge capacity, and these are very important parameters when considering the applicability of polymer films to switching devices [4].

In polypyrrole containing the large surfactant molecules, dodecyl benzene sulfonate (DBS), the DBS anions remain immobile inside the film during cycling. Therefore, cation transport is expected to be the dominant process during redox cycling. Although the motion of cations is the most important component, there is a significant anion contribution to the ionic transport [5]. In the present study we found that this anion contribution is more pronounced in the case of highly concentrated cycling electrolytes.

For successful use of polypyrrole films in artificial muscles a precise understanding and control over which ionic species are mobile during the actuation is important [5]. In the present study we demonstrated that the concentration of the supporting electrolyte not only determines the moving ionic species but

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also strongly influence the rate of ion transport during the redox process.

The redox kinetics of conducting polymers has been investigated by many electrochemical methods such as ac impedance spectroscopy, chronocoulometry, cyclic voltammetry, chronoabsorptometry and chronoamperometry. In this study we have used cyclic voltammetry to investigate the counter ion motion during redox process of PPy/DBS films in NaCl electrolytes by treating the motion as diffusion and quantify it with diffusion coefficient using the techniques adopted by West et al. to study diffusion in intercalation electrode materials [6].

2. Methodology

The voltammetric cycling of polymer films is a sensitive probe of interactions in the materials: the shapes and positions of the oxidation and reduction peaks contain both ‘finger print’ information about the nature of the ions and solvents present, and information about the sign of the charge of the dominantly mobile ion. It is possible to form PPy films with sharp peaks in cyclic voltammograms from aqueous solution containing large surfactant molecules such as dodecyl benzene sulfonate [5].

By cycling repeatedly, the reversibility of the process can be followed. The voltammogram can also give information about the kinetics of the process, and the change of the voltammogram as a function of the sweep rate can be analysed in terms of the effective diffusion coefficient of the ions in the polymer film, as was previously done for inorganic insertion materials [6]. This treatment is based on the assumption that the interfacial composition of the electroactive material is uniquely determined by the electrode potential, and that transport from the electrode/electrolyte interface into the bulk material is governed by Fickian diffusion. In [6] results were derived for planar, cylindrical and spherical diffusion geometries, as well as for two representative composition/potential relationships—a linear correlation and a step function (applicable to two-phase transitions).

In the present context, transport in PPy/DBS coatings will be treated as planar diffusion, and in the potential range investigated here a linear relationship between charge insertion and potential during the cathodic scan will be assumed. Under these assumptions, the relationship between cathode utilization U (defined as the ratio of the charge accumulated in the electrode relative to the maximal charge that can be accumulated under equilibrium conditions), and sweep rate α is derived by West et al. [6] as $U = 4/3\sqrt{(E_1 - E_2)/\pi\tau\alpha}$, where $E_1 - E_2$ is the potential window used for the scan and τ is the time constant for diffusion in the electrode. Assuming Fickian diffusion, plots of U versus $1/\sqrt{\alpha}$ for PPy/DBS films cycled in NaCl aqueous electrolyte should show that U is approximately proportional to $1/\sqrt{\alpha}$ down to a critical sweep rate, and at lower sweep rates U becomes independent of α . From this plot, τ can be determined from the critical sweep rate marking the transition between the two linear regimes. Then the effective diffusion coefficient of ion movements in the polymer film can be obtained using the relation $D = l^2/\tau$, where l is the length of diffusion. If the diffusion is assumed to occur across the film uniformly, l will correspond to the thickness of the film.

PPy films were galvanostatically electro polymerised on Pt wire electrodes with an effective area of 0.157 cm^2 in a solution containing 0.05 M distilled pyrrole monomer and 0.05 M NaDBS salt. The thickness of the coatings was determined by the amount of charge passed during the synthesis (160 mC cm^{-2} yields a $1 \mu\text{m}$ thick coating). Ag/AgCl was used as the reference electrode. Cycling experiments were done in aqueous NaCl electrolytes with concentrations of 0.1 M, 1.0 M, 3 M and 5 M.

3. Results and discussion

A series of cyclic voltammograms at different sweep rates for $5 \mu\text{m}$ thick PPy/DBS films cycled in NaCl electrolytes having concentrations 0.1 M, 1 M and 3 M, respectively, at 25°C are shown in Fig. 1a–c. To avoid the problem caused by ‘memory effects’ or ‘slow relaxation’, the sweep rate test was done on each film after 10 initial conditioning cycles. In order to facilitate comparison of all the curves the current values were divided by the sweep rates. In the resulting differential capacity versus voltage diagrams, the area under a curve is a direct measure of the charge that is cycled in and out of the film during redox cycling. Significant changes are observed in the cyclic voltammograms with the sweep rate. The scan rate significantly affects the positions of nearly all peaks and this fact proves the important role of kinetic factors in the redox process. The figures reveal that the cathodic peaks in all graphs become progressively broader and shift to more negative potentials with increasing scan rate. This implies that the cations and anions are no longer able to participate fully in the doping/dedoping process at high sweep rates. The second oxidation peak at 0.2 V becomes more prominent when the concentration of the cycling electrolyte is increased. Although the normalised voltammograms converge towards a common shape at low sweep rates (most clearly seen in the set of voltammograms obtained in the dilute electrolyte), this limiting curve still shows a pronounced asymmetry between the anodic and cathodic branches, demonstrating an inherent hysteresis in the electrochemistry of the PPy/DBS system. In case of diffusion limited ion insertion into an otherwise unchanged material, the only expected effect of changing the electrolyte concentration is a Nernstian movement of peak potentials: peaks due to cation expulsion should move towards more positive potentials, whereas peaks due to anion insertion should move in the negative direction. The diffusion kinetics itself is not expected to be influenced by the electrolyte concentration. The characteristic changes with concentration in the shape of the anodic branch of the voltammograms in Fig. 1a–c are consistent with the first anodic peak corresponding to cation (Na^+) expulsion, whereas the other anodic peak (most clearly seen in Fig. 1c) corresponds to anion (Cl^-) insertion. The narrow cathodic peak corresponds to both insertion of cations and the expulsion of anions [5].

When the PPy/DBS film is cycled in 0.1 M NaCl, at high sweep rates the minimum potential has to be increased to -1 V from the usual value of -0.85 V in order to obtain fully developed cathodic peak. In contrast, in the cyclic voltammograms in 1 M and 3 M NaCl, the cathodic peaks are fully developed before the minimum potential of -0.85 V is reached at all sweep rates. These observations indicate that the redox process of the

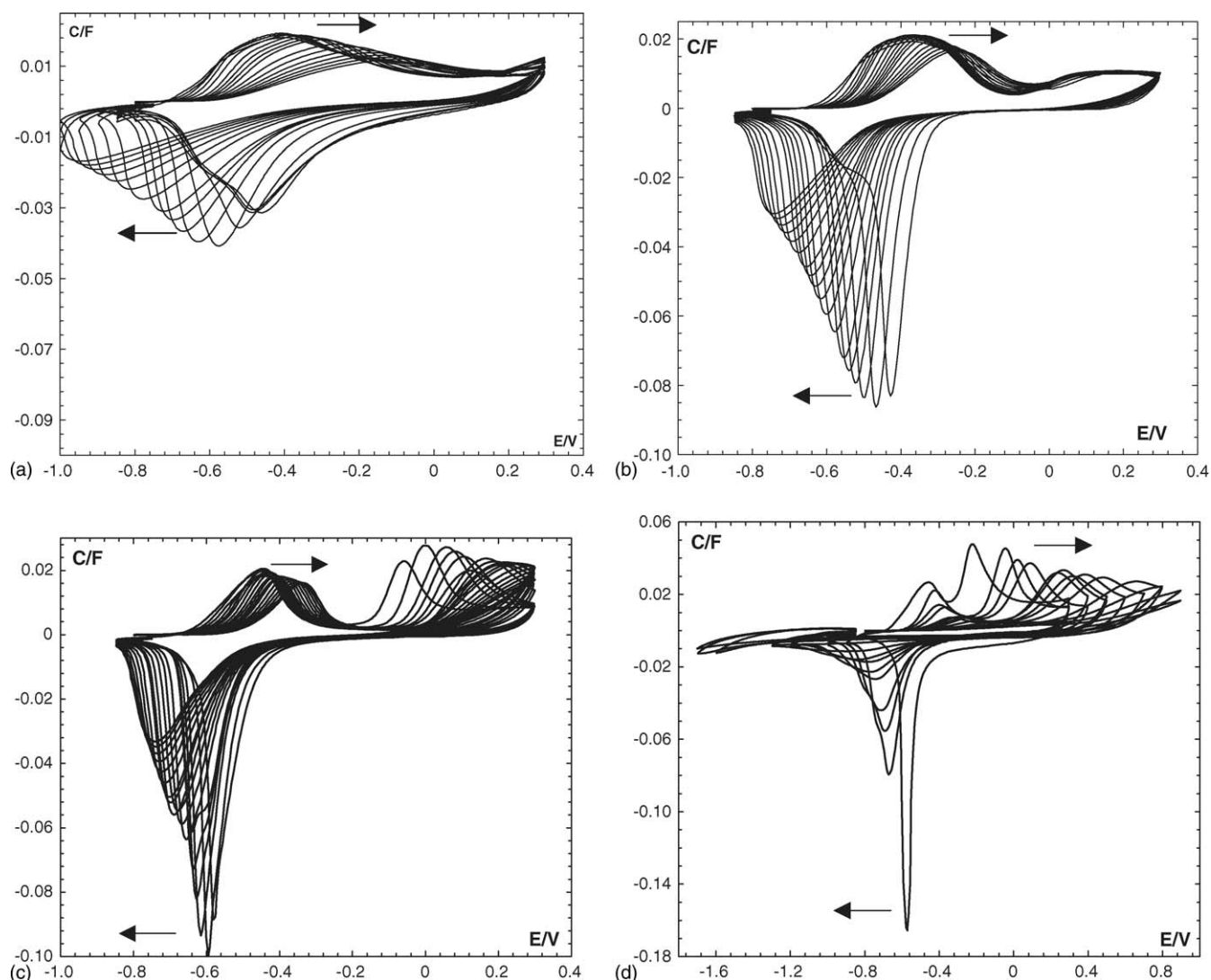


Fig. 1. PPy/DBS film cycled at different sweep rates: (a) 1 mV s^{-1} , 3 mV s^{-1} , 5 mV s^{-1} , 10 mV s^{-1} , 20 mV s^{-1} , 40 mV s^{-1} , 60 mV s^{-1} , 80 mV s^{-1} , 100 mV s^{-1} , 150 mV s^{-1} , 200 mV s^{-1} , 250 mV s^{-1} , 300 mV s^{-1} , 350 mV s^{-1} , 400 mV s^{-1} and 450 mV s^{-1} in 0.1 M NaCl at 25°C . Thickness— $5 \mu\text{m}$. (b) 5 mV s^{-1} , 10 mV s^{-1} , 20 mV s^{-1} , 40 mV s^{-1} , 60 mV s^{-1} , 80 mV s^{-1} , 100 mV s^{-1} , 150 mV s^{-1} , 200 mV s^{-1} , 250 mV s^{-1} , 300 mV s^{-1} , 350 mV s^{-1} , 400 mV s^{-1} , 450 mV s^{-1} , 500 mV s^{-1} , 550 mV s^{-1} , 600 mV s^{-1} , 700 mV s^{-1} , 800 mV s^{-1} , 900 mV s^{-1} and 990 mV s^{-1} in 1 M NaCl at 25°C . Thickness— $5 \mu\text{m}$. (c) 10 mV s^{-1} , 20 mV s^{-1} , 60 mV s^{-1} , 80 mV s^{-1} , 100 mV s^{-1} , 150 mV s^{-1} , 200 mV s^{-1} , 250 mV s^{-1} , 300 mV s^{-1} , 350 mV s^{-1} , 400 mV s^{-1} , 450 mV s^{-1} , 500 mV s^{-1} , 550 mV s^{-1} , 600 mV s^{-1} , 700 mV s^{-1} , 800 mV s^{-1} , 900 mV s^{-1} and 990 mV s^{-1} in 3 M NaCl at 25°C . Thickness— $5 \mu\text{m}$. (d) 1 mV s^{-1} , 5 mV s^{-1} , 10 mV s^{-1} , 20 mV s^{-1} , 40 mV s^{-1} , 60 mV s^{-1} , 80 mV s^{-1} , 100 mV s^{-1} , 150 mV s^{-1} , 250 mV s^{-1} , 350 mV s^{-1} , 450 mV s^{-1} and 550 mV s^{-1} in 3 M NaCl at 25°C . Thickness— $50 \mu\text{m}$.

film in highly concentrated electrolytes is faster. However, the second oxidation peak in 3 M NaCl gradually diminishes with the sweep rate for rates higher than 500 mV s^{-1} . In addition, to observe the second oxidation peak during high rate scans, the oxidation potential must be extended to higher values. Fig. 1d shows the cyclic voltammograms of a thicker $50 \mu\text{m}$ PPy/DBS film cycled in 3 M NaCl at 25°C in an increased potential window from -1.6 V to 1.0 V . However, during low rate scans the potential window was limited to the reversible redox regime, -0.85 to 0.3 V , to avoid over oxidation. The potential window was then gradually increased for higher rate scans. When the PPy/DBS film was cycled in 0.1 M NaCl the cyclic voltammograms of 1 – 10 mV s^{-1} coincided with each other indicating that equilibrium has been reached. But when cycled in 3 M NaCl , the equilibrium has not been reached even for sweep rates

close to 1 mV s^{-1} (Fig. 1d), indicating that although the reaction rates may be faster in the concentrated electrolytes, the internal reorganisations of the polymer structure that accounts for the hysteresis still occur at a very long time scale.

Fig. 2a and b shows the electrode charges during the cathodic sweep of a PPy/DBS film as a function of the inverse square root of the sweep rate at different temperatures for 0.1 M and 1 M NaCl , respectively.

Only a small amount of capacity is lost during the 10–50 deep cycles normally conducted on a successful electrode preparation. However, to avoid systematic errors due to these losses, the films were cycled in a random sequence of the different sweep rates. As can be seen from the figures, only a small part of the expected linear regime at high sweep rates could be measured. This is mainly because the uncompensated ohmic drop in

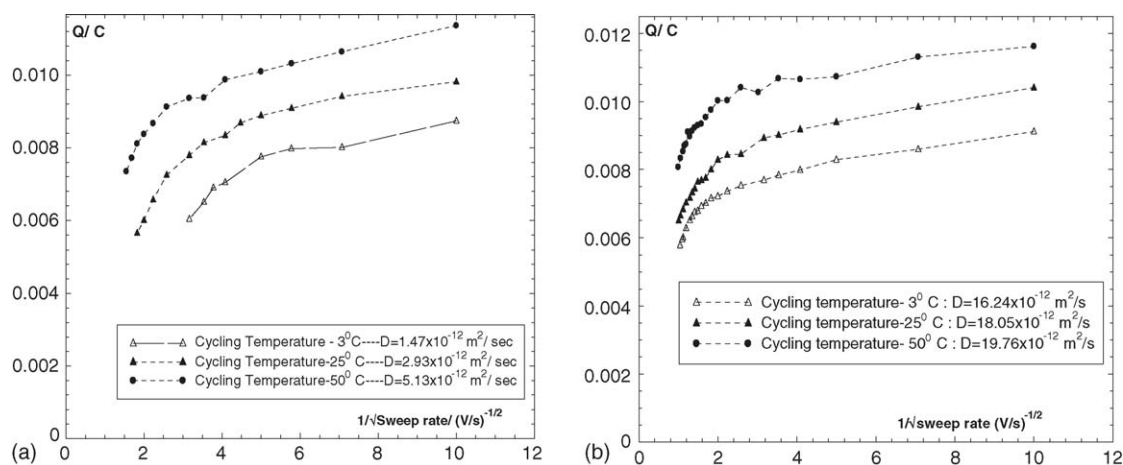


Fig. 2. The electrode charge vs. inverse square root of the sweep rates for a PPy/DBS film cycled in electrolytes: (a) 0.1 M NaCl and (b) 1 M NaCl at different temperatures. Film thickness—5 μm .

the electrolyte severely distorts the results at higher sweep rates. The intersection of the tangent to the curve through the origin and a linear approximation to the data obtained at low sweep rates is used as a measure for the transition from infinite to finite diffusion regimes. Table 1 shows the calculated apparent diffusion coefficients of the PPy/DBS films at different electrolyte temperatures and concentrations.

The effective diffusion coefficient at 25 $^{\circ}\text{C}$ for the film cycled in 1 M NaCl is nearly 7 times higher than that of the film cycled in 0.1 M NaCl. It was also found that in 0.1 M NaCl the ratios of the diffusion coefficients at different temperatures is nearly equal to the ratios of the viscosity of water at the same temperatures. These results indicate that in electrolytes with low concentration, diffusion in the electrolyte rather than diffusion in the polymer film may be the limiting kinetic factor. The activation energy of the PPy/DBS film cycled in 0.1 M NaCl is 8.56 kJ mol^{-1} and when cycled in 1 M NaCl, it is only 1.35 kJ mol^{-1} .

The graph of the electrode charge during the cathodic sweep versus the inverse square root of sweep rate plotted using the results in Fig. 1c for the film with thickness 5 μm cycled in 3 M NaCl was almost flat and did not show any turning point (not shown). Because of this we could not assign a diffusion coefficient of counter ions in PPy/DBS film with the thickness 5 μm

Table 1
Effective diffusion coefficients for PPy/DBS films in NaCl electrolyte of different concentrations at different temperatures

Concentration (M)	Temperature ($^{\circ}\text{C}$)	D ($\text{m}^2 \text{s}^{-1}$)
0.1	3	1.5×10^{-12}
	25	2.9×10^{-12}
	50	5.1×10^{-12}
1	3	16×10^{-12}
	25	18×10^{-12}
	50	20×10^{-12}
3	25	55×10^{-12}

Thickness of the film used for 0.1 M and 1 M electrolytes is 5 μm and for the 3 M electrolytes it is 50 μm .

cycled in 3 M NaCl. This implies that the diffusion coefficient in 3 M NaCl is some how higher than the diffusion coefficients we found earlier in 0.1 M NaCl and 1 M NaCl. Hence a 50 μm PPy/DBS film was used to determine the diffusion coefficient in 3 M electrolyte. The plot of Q versus $1/\sqrt{\alpha}$ for this film corresponding to the results in Fig. 1d is shown in Fig. 3. The value for the diffusion coefficient in 3 M NaCl obtained from this plot is $55 \times 10^{-12} \text{m}^2 \text{s}^{-1}$. Attempt to make a similar analysis in 5 M NaCl failed because the cyclic voltammograms were not well defined at high sweep rates.

The Fig. 4 shows the U versus $1/\sqrt{\alpha}$ curves for PPy/DBS films of different thicknesses cycled in 0.1 M NaCl electrolyte. The diffusion coefficients calculated are shown in the graph itself. As can be seen the time constant does not change as much as expected in order to yield a thickness independent diffusion coefficient. This indicates that diffusion in the electrolyte may be an equally important limiting factor as solid-state diffusion for thin PPy/DBS film cycled in dilute electrolytes.

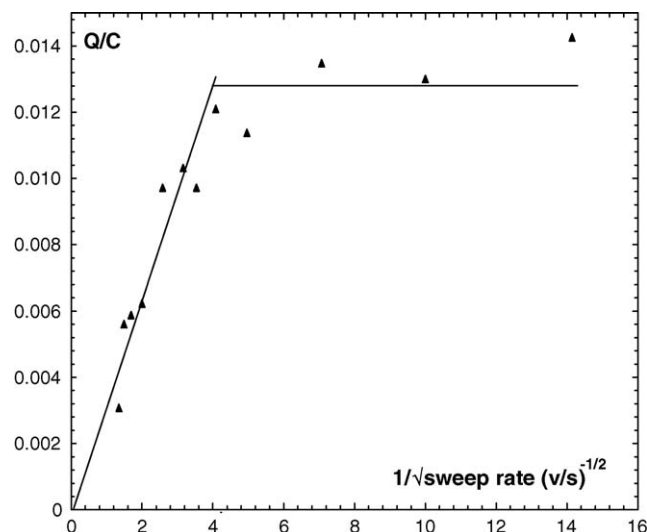


Fig. 3. Plot of Q vs. $1/\sqrt{\alpha}$ for a 50 μm thick PPy/DBS film cycled in 3 M NaCl at 25 $^{\circ}\text{C}$.

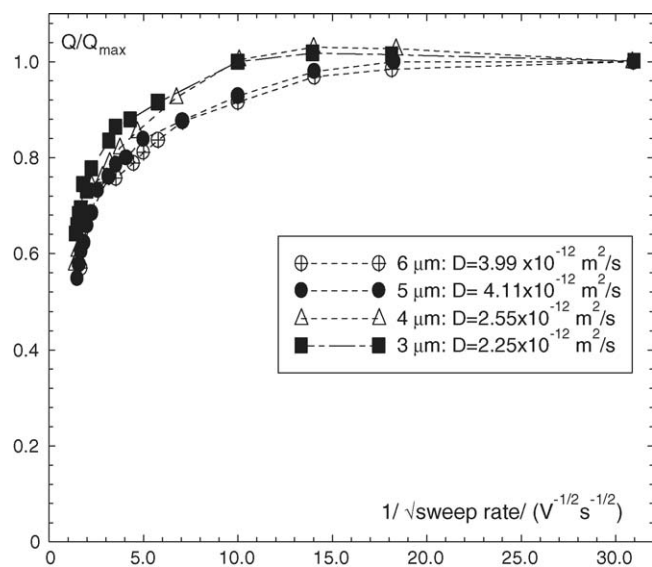


Fig. 4. U vs. $1/\sqrt{\alpha}$ graph for PPy/DBS films of different thicknesses at 25 °C.

4. Conclusion

Polypyrrole conducting polymer films doped with large immobile anion dodecyl benzene sulfonate have been used to investigate the mobility of counter ions during redox processes in aqueous NaCl electrolytes. The mobility of counter ions determines the speed of response when using these films as electrodes in batteries or in artificial muscles. The results show the complex character of the doping process and the importance of the electrolyte concentration in determining the mobility of counter ions. The value of the effective diffusion coefficient of dopant ions was

found to depend strongly on the electrolyte concentration—the values determined at 25 °C in 0.1 M, 1 M and 3 M NaCl are $3 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$, $20 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ and $55 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$, respectively. For thin electrodes in diluted electrolytes diffusion in the electrolyte may be a just as important limiting factor as solid-state diffusion. The finding that the speed of counter ion diffusion in PPy/DBS is dependent on the concentration of the electrolyte is somewhat surprising, but reflects the fact that the bathing electrolyte to a large extent controls the composition of the polymer coating: in dilute electrolytes the polymer may take up water due to osmotic forces, whereas in concentrated electrolytes it may take up additional electrolyte salt.

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