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Properties of electrochemically synthesized polymer electrodes
Part VII: Kinetics of poly-3-methylthiophene in lithium cells

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The electrochemical behaviour of poly-3-methylthiophene is discussed in comparison with that of other parent polymer electrodes, such as polythiophene and polydithiophene, on the basis of voltammetric and impedance response analysis. The results indicate that the kinetics of the redox processes of the three electrodes are controlled by ion diffusion into the polymer structure and that poly-3-methylthiophene is the most suitable material for the use as cathode in lithium, rechargeable batteries.

1. Introduction

Among the various electrochemically synthesized conducting polymers, the polythiophenes have stimulated the interest of many authors since they are attractive candidates as new electrode materials in advanced electrochemical devices [1]. For instance, polythiophenes may be used in electrochromic devices – as originally established by Garnier and coworkers [2] and also confirmed in our laboratory [3] – or in lithium batteries, as initially proposed by Wudl and co-workers [4], by Kaneto *et al.* [5] and by Diaz and co-workers [6, 7].

In previous work [8–10] we have shown that the p-doping/undoping (redox) processes of polythiophenes are reversible and thus confirmed that these polymers are indeed promising positive electrodes in rechargeable, organic electrolyte lithium batteries. However, not much attention has been so far devoted to the study of these processes and to the investigation of the characteristics of the interfaces of polythiophene electrodes in contact with liquid, organic electrolytes. On the other hand, the definition of the interfacial properties appears of fundamental importance, especially for understanding the mechanism of the ion diffusion processes which control the rate of the electrochemical response of the polymer electrodes [1, 9].

In an attempt to fill this gap, we have carried out a study of the electrochemical behaviour of poly-3-methyl-thiophene (PMeT) in comparison with that of other parent polymers, namely polythiophene (pT) and poly-dithiophene (pDT). The results of this study are reported and discussed in this work.

2. Experimental details

All the polymers examined were obtained by electrosynthesis on a platinum support by oxidation at controlled current densities of the monomers (i.e. thiophene, 2-2′ dithiophene and 3-methyl-thiophene, respectively) in a solution of 0.5 M $LiClO_4$ in propylene carbonate. A three-electrode synthesis cell, having separate compartments was used. The working (Pt) and the counter (Li) electrode were housed in one compartment while the reference (Li) electrode was situated in the other. All the potential values were then referred to lithium.

Critical for the electrosynthesis was the purity of the starting materials (monomer and electrolyte solution). Therefore, all the chemical compounds, reagent-grade products, were carefully purified before use.

Thiophene and 3-methylthiophene (Aldrich-Chemie), reagent grade product, were distilled under vacuum. 2-2′ dithiophene (Aldrich-Chemie), was dissolved in hexane and then passed through activated alumina. Propylene carbonate was distilled under vacuum. Lithium perchlorate (Fluka), was purified by fusion under vacuum at 250 °C. The best results in terms of doping level and stability were obtained for freshly prepared solutions.

The electrosynthesis of polymers, the cell assembly and the related tests were all carried out in a controlled atmosphere dry box (humidity content less than 10 p.p.m.).

The thickness of the polymer films grown on platinum substrates was controlled by monitoring the grafting charge and it is expressed as coverage factor Γ. Typically, Γ values ranging from 7×10^{-7} to $5 \times 10^{-6}\,mol\,cm^{-2}$, corresponding to a thickness of 1 to 5 μm, have been used for the electrochemical tests. The electrochemical characterization was carried out in a three-electrode cell using Li counter and Li reference electrodes, and a solution 0.5 M $LiClO_4$ in propylene carbonate (simply indicated in this work as $LiClO_4$–PC).

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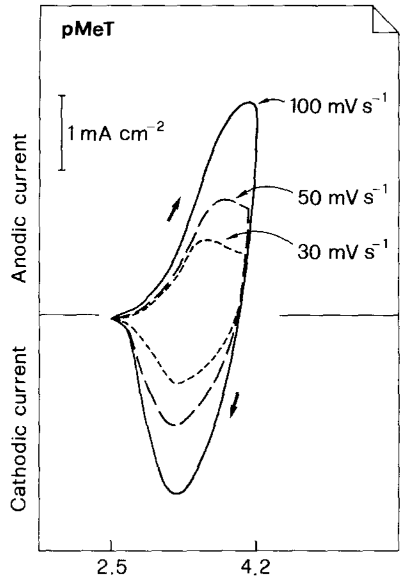

Fig. 1. Cyclic voltammetry of a pMeT/Pt electrode in the $LiClO_4$–PC solution at various scan rates and at room temperature. Li reference electrode.

Cyclic voltammetry curves were obtained using an AMEL mod. 551 potentiostat coupled with an AMEL mod. 567 function generator and registered with a YEW mod. 3022 X–Y recorder.

The frequency response analysis (FRA) was carried out using a Solartron mod. 1250 analyser coupled with a Solartron mod. 1286 electrochemical interface.

The lithium batteries were realized by facing a lithium strip (Foote Mineral Co.) with the selected electrodeposited polythiophene film in the $LiClO_4$–PC electrolytic solution.

3. Results and discussion

3.1. *Voltammetric analysis*

The p-doping/undoping redox process of heterocyclic polymers generally involves the oxidation (and reduction) of the polymers and compensation of charge via diffusion of ions from the electrolyte. In the case under study, one may consider the general scheme:

$$P + yX^- \rightleftharpoons P(X)_y + ye^- \qquad (1)$$

where y indicates the amount of charge involved (often y is also called doping level), X is the electrolyte anion (here ClO_4^-) and P is the sleected polymer, i.e. poly-3-methyl-thiophene (pMeT), poly-dithiophene (pDT) and polythiophene (pT), respectively.

Figure 1 illustrates the cyclic voltammograms at various scanning rates of a pMeT electrode electrodeposited on platinum. The voltammograms show that the electrode can be repeatedly cycled with good reproducibility. The anodic and the cathodic waves remain well defined and the integrated charge under the reduction wave, Q_c, approaches that under the oxidation wave, Q_a. Consequently, a high coulombic efficiency $\eta = Q_c/Q_a$ is obtained under these conditions, as indicated in Table 1, where the voltammetric data of various pMeT/Pt electrodes having different coverage factors are summarized.

Table 1. Voltammetric data related to the oxidation process of pMeT/Pt electrodes in the $LiClO_4$–PC solution at room temperature

Coverage factor $\Gamma \times 10^{-7}$/mol cm^{-2}	*Scan rate* v/mV s^{-1}	*Doping level* y/%	*Efficiency* η/%
9	30	28	98
	50	26	
	100	23	
20	30	22	98
	50	21	
	100	18	
54	30	11	95
	50	10	
	100	8	

It may be useful to point out that the doping level y is defined as the percentage of moles of the doping anion (X^-) over moles of the monomeric unit. The numerical values are obtained considering that the moles of X^- (here ClO_4^-) are expressed by the cyclable charge, Q_{cycl}, which in turn is given by the ratio between the number of cyclable Faradays and the number of electrons n involved in the electrochemical process (here $n = 1$). Accordingly, the moles of monomeric unit are given by the ratio of the difference between the number of Faradays passed for the entire process and the number of cyclable Faradays over the number of electrons for the entire electrochemical process (here $n = 2$). Therefore, the doping level y may be readily obtained by the expression

$$y = \frac{2Q_{cycl}}{Q_{tot} - Q_{cycl}} \qquad (2)$$

Table 1 shows that the achievable doping level, y, (i.e. the maximum cycling charge) depends upon scan rate and sample thickness. This is an indication that the kinetics of the redox process of pMeT are controlled by ion diffusion into the bulk of the polymer, as generally observed for heterocyclic polymer electrodes [1, 9, 11]. In fact, it is reasonable to expect that under diffusion-controlled kinetics, the amount of cyclable charge varies upon variation of scan rate and sample thickness, as indeed confirmed by the data of Table 1.

Figures 2 and 3 illustrate the cyclic voltammograms of pT/Pt and of pDT/Pt electrodes, respectively, obtained under experimental conditions similar to those used for the pMeT/Pt electrode. The voltammetric behaviour of the three polymer electrodes is compared in Table 2 in terms of maximum achievable doping level, y, and peak voltage separation, ΔE_p.

This table shows some interesting features. First, the peak voltage separation increases in all cases upon increasing scan rate, this revealing that the electrochemical reversibility is approached only at low rates. This again may be related to the slow diffusion of the counterions in the polymer structure.

Furthermore, from Table 2 it is seen that while the

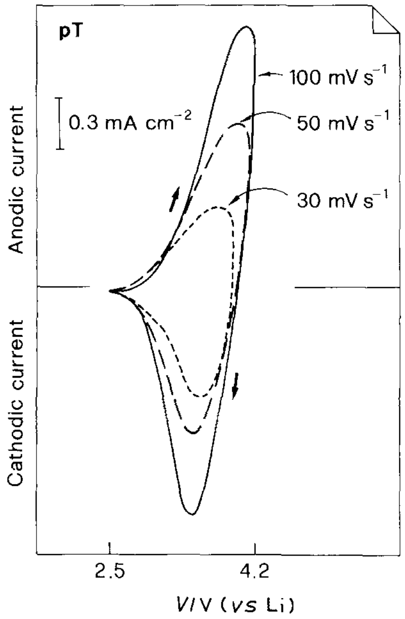

Fig. 2. Cyclic voltammetry of a pDT/Pt electrode in the $LiClO_4$–PC solution at various scan rates and at room temperature. Li reference electrode.

achievable doping levels are comparable for pMeT and pDT, much lower values are obtained for pT. This may be related to the fact that polymers derived from dithiophene and methylthiophene are expected to be more regularly chained via $\alpha - \alpha'$ links. Such a steric organization favours faster charge transport and thus higher doping level than in the case of thiophene-derived polymers in accordance with the mechanism discussed in details by Tourillon [11].

The above aspects are quite relevant in view of the practical application of these polymer electrodes in lithium batteries. In fact, the capacity of such batteries is directly related to the doping level while their power is directly related to the cycling rates. Therefore, the data of Table 2 show that polythiophenes in general are not particularly suitable as polymer electrodes for high-capacity, high-power batteries and that, if any of them must be used, the choice should be directed to pMeT or to pDT, which show the lowest percentage of peak separation and the lowest decay in doping level upon increase of scan rate.

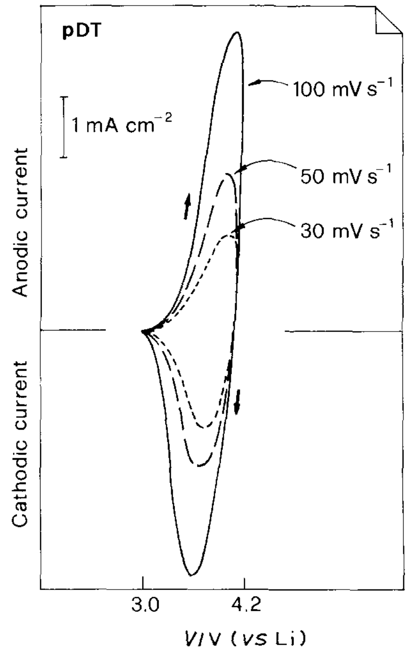

Fig. 3. Cyclic voltammetry of a pT/Pt electrode in the $LiClO_4$–PC solution at various scan rates and at room temperature. Li reference electrode.

Table 2. Voltammetric data related to the redox process of pMeT/Pt, pDT/Pt and pT/Pt electrodes in the $LiClO_4$–PC solution at room temperature ($\Gamma = 9 \times 10^{-7}$ mol cm^{-2})

Electrode	*Scan rate* v/mV s^{-1}	*Peak voltage separation* ΔE_p/mV	*Doping level* y/%
pMeT	30	380	28
	50	605	26
	100	775	23
pDT	30	275	28
	50	350	23
	100	600	22
pT	30	275	13
	50	350	12
	100	600	9

This has been experimentally verified by testing the performance of cell of the type Li/$LiClO_4$–PC/P–Pt where P was alternatively pMeT, pDT or pT. Figure 4 illustrates typical charge-discharge cycles of these cells and the comparison clearly reveals that pMeT and pDT have comparable performance which remains for both higher than that of pT. This is also confirmed by Table 3 which compares the values of energy density of the three polymer electrodes, calculated on the basis of the maximum cyclable charge and the average discharge voltage.

3.2. *Frequency response analysis*

Considering the results of the previous section, the

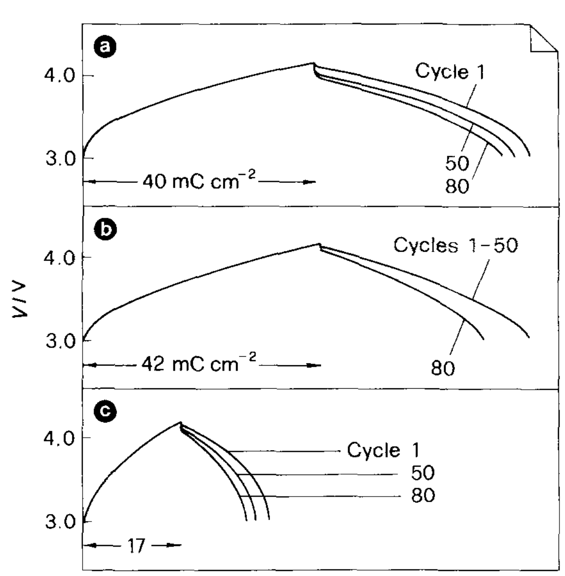

Fig. 4. Typical galvanostatic (0.5 mA cm^{-2} charge current density, 0.5 mA cm^{-2} discharge current density) cycles of the Li/$LiClO_4$–PC/P–Pt battery at room temperature, where P is pMeT (a) pDT (b) and pT (c). The number of cycles is indicated in the figure.

Table 3. Values of energy density of lithium–polymer electrode systems calculated on the basis of maximum cyclable charge and average discharge voltage

Electrodic system	*Specific capacity* /Ah kg^{-1}	*Energy density* /Wh kg^{-1}
Li–pMeT	54	162
Li–pDT	52	156
Li–pT	34	102

kinetics of the most promising electrodes, i.e. pMeT and pDT, were further investigated by frequency response analysis (FRA). This is a technique which has been proved to be very valuable in defining the kinetic behaviour of electrochemical reactions in general [12] and of the redox processes of heterocyclic polymers in particular [13, 14].

In fact, if the analysis is extended over a sufficiently wide frequency range, the different phenomena associated with the polymer/electrolyte, interface can be separated and evaluated. The FRA of pDT electrodes was discussed in a previous work [9] and, therefore, here we focus our attention on results related to the pMeT electrode/$LiClO_4$–PC interface only. The impedance analysis was carried out on a cell having a pMeT/Pt working electrode, a Li counter electrode and a Li reference electrode in the 0.5 M $LiClO_4$–PC solution. An electrochemical interface was used in order to determine the impedance response of the single pMeT interface at any desired polarization against the lithium reference.

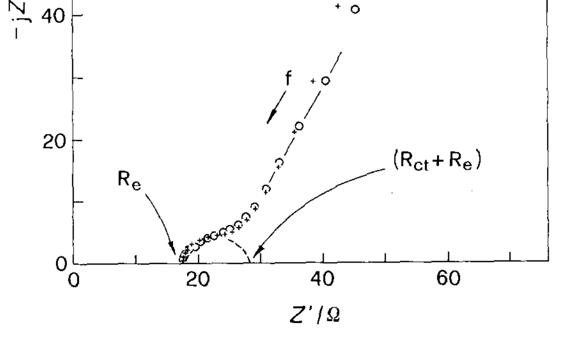

Fig. 5. Impedance response of the pMeT electrode in the $LiClO_4$–PC solution. Electrode coverage: $\Gamma = 9.8 \times 10^{-7}$ mol cm^{-2}; doping level $y = 15\%$. Frequency range: 0.1–40 kHz. (O) fitted data; (+) experimental data.

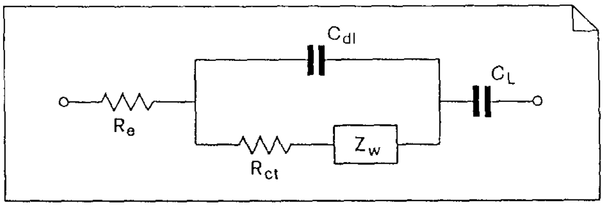

Fig. 6. Modified Randles equivalent circuit for thin film polymer electrodes, where R_e is the resistance of the electrolyte, R_{ct} is the charge transfer resistance, C_{dl} is the double layer capacitance, Z_w is the Warburg impedance and C_L is the limiting capacitance.

Figure 5 illustrates the impedance response of the pMeT electrode over the entire frequency range of interest. As extensively discussed by Huggins and coworkers [15] and by Smyrl and coworkers [16], the impedance response of polymer electrodes may be considered similar to that presented by intercalation electrodes and thus interpreted on the basis of the modified Randles circuit illustrated in Fig. 6. In this circuit R_e is the resistance of the electrolyte between the working and the reference electrodes, R_{ct} is the charge transfer resistance of the faradaic process, C_{dl} is the double-layer capacitance of the polymer/electrolyte interface, Z_w is the Warburg impedance and C_L is the limiting capacitance, in the nonfaradaic regimes. The impedance parameters may be obtained by examining the response of Fig. 5 in the various relevant frequency regions. The high-frequency region, say in the high kHz range, identifies the bulk properties of the electrolyte and the intercept with the real axis (Z') provides the value of the electrolyte resistance R_e.

The medium and low frequency regions are the one of major interest in this work since associated with the interfacial parameters. In the medium frequency region (i.e. in the kHz range) the expected response in the $jZ'' - Z'$ diagram is a semicircle, whose time constant is given by the product of the double layer capacitance C_{dl}, and the charge-transfer resistance, R_{ct}, the value of the latter being given by the intercept with the real axis.

In the low-frequency region, i.e. in the Hz range, the impedance becomes controlled by diffusion and thus the response is here representative of the mass transfer parameters of the redox process. In the $jZ'' - Z'$ complex plane, the response assumes a linear behaviour with a frequency-independent phase angle of $\pi/4$, represented in the equivalent circuit of Fig. 6 by the Warburg impedance element Z_w. Finally, when the analysis is extended to very low frequency values, e.g. in the mHz range, and if the thickness of the electrode, L, is sufficiently small to determine the so-called "finite length" condition [15, 16], the diffusion process will be progressively limited in favour of a charge accumulation into the polymer host. Accordingly, the a.c. impedance approaches a purely capacitive response with a phase angle $\pi/2$.

The kinetic parameters of the redox process of the pMeT electrode in the $LiClO_4$–PC electrolyte can then be evaluated on the basis of the described impedance analysis. We first examine the medium frequency range and notice that in the experimentally obtained response of Fig. 5, the semicircular arc does not completely close on the real axis as would be expected for an idealized charge-transfer process. On the other hand, this is not surprising but rather expected on the basis of the voltammetric results which clearly indicate

Table 4. Kinetic parameters of the pMeT electrode in the LiClO$_4$–PC electrolyte at room temperature, obtained from the frequency response analysis. ($\Gamma = 9.8 \times 10^{-7}$ mol cm^{-2}; y = 15%)

Charge transfer resistance R_{ct}/Ω	*Double layer capacitance* C_{dl}/F cm^{-2} × 10^4	*Limiting capacitance* C_L/F cm^{-2} × 10^2	*Ion diffusion coefficient* D/cm^2 s^{-1} × 10^9
6.6	3.00	2.2	1.17

that the redox process of pMeT is controlled by the diffusion of the counterions. However, the charge transfer resistance, R_{ct}, and the double layer capacitance, C_{dl}, may still be evaluated by using a suitable fitting program. We used in this case a modified version of the Boukamp's program [17]. As demonstrated in Fig. 5, the fitted data follows in a very satisfactory fashion the experimentally obtained impedance response.

Under these conditions, one may evaluate from the maximum of the medium-frequency semicircle, the characteristic relaxation frequency

$$f_c = \frac{1}{R_{ct} C_{dl}} \quad (3)$$

from which, knowing the value of R_{ct}, the interfacial double layer capacitance can also be determined. The data are summarized in Table 4.

From this table it is seen that the double layer capacitance, C_{dl}, determined on the basis of Equation 3, is of the order of 300 μF cm^{-2}. This value is much larger than the typical values of electrode/electrolyte double layer capacitance, expected to be in the range 20 and 30 μF cm^{-2} [18]. However, this difference may be explained by the fact that electrosynthesized polymer electrodes generally present a very rough surface and thus the real electrode/electrolyte contact area can be quite different from the superficial geometric area, whose value was used in Equation 3. Therefore, assuming this explanation as plausible, one can use the comparison between the C_{dl} value obtained by Equation 3 and that usually associated with an electrochemical interface to estimate the ratio of effective and geometrical areas. In the case under study here, the effective contact area is at least ten times larger than the superficial geometric area. This evaluation is not unrealistic since the electrochemical synthesis produces polymer films with highly disordered surfaces; indeed, comparable real to geometrical surface ratios close to 10 have been found for other polymer electrode/organic liquid electrolyte interfaces [14, 19].

Further information on the kinetics of the redox process of the pMeT electrode may be obtained from the analysis of the low-frequency range of the impedance response, which is related to mass transfer and limiting capacitance effects. Figure 7 illustrates the response of the pMeT electrode in the 25 Hz to 0.01 Hz frequency range. As expected by the equivalent circuit of Fig. 6, the impedance response approaches a purely capacitive behaviour at very low frequencies (f < 1 Hz) reflecting the charge saturation limits. This effect, which may be associated to the formation of double layers of static charge, is typical for the high-porous thin-film polymer electrodes [13, 14] and is also revealed by cyclic voltammetry analyses [19, 20]. The associated capacitance, C_L, often called "limiting capacitance" is related to the limiting resistance R_L (obtained by extrapolating the $\pi/2$ phase angle data to the real axis [15, 16] and to the ion diffusion coefficient, D, by the equation

$$C_L = \frac{L^2}{3DR_L} \quad (4)$$

The impedance data, evaluated in the basis of this equation, provided the numerical results reported in Table 4.

The limiting capacitance is found to be C_L = 22 mF cm^{-2}, a value comparable to that usually found for heterocyclic polymers [14, 19]. From this limiting capacitance value the ion diffusion coefficient in the pMeT electrode was calculated to be $D = 1.17 \times 10^{-9}$ cm^2 s^{-1}. Diffusion coefficients in the range of 10^{-9}–10^{-10} cm^2 s^{-1} are usually representative of slow ion mobility. Therefore, the impedance analysis, in agreement with the voltammetric result, confirms that the diffusion of the compensating ionic charge in the polymer structure may considerably limit the kinetics of the redox processes of the pMeT electrodes. This is an important conclusion in view of the application of these electrodes in practical electrochemical devices. Certainly, polythiophenes do not appear suitable for the development of high-rate batteries nor for fast-response electrochromic devices. However, polymethylthiophene may still be of considerable technological

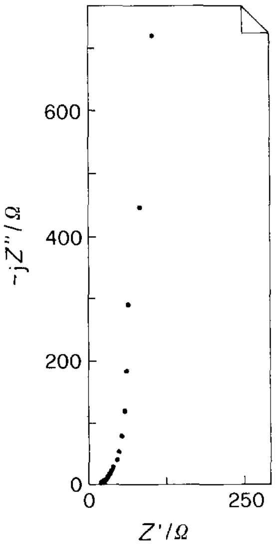

Fig. 7. The low frequency impedance response of the pMeT electrode in the LiClO$_4$–PC solution. Electrode coverage: $\Gamma = 9.8 \times 10^{-7}$ mol cm^{-2}; doping level y = 15%. Frequency range: 0.01–25 Hz.

interest if used in devices where high-voltage and sharp colour contrast are more crucial factors than rate, such as memory back-up batteries or smart windows. The feasibility of these proposed applications is currently under test in our laboratory.

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