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Polymers and copolymers of pyrrole and thiophene as electrodes in lithium cells

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The performance of pyrrole and thiophene polymer electrodes in lithium cells has been examined in the lithium perchlorate–propylene carbonate electrolyte by cyclic voltammetry. Polypyrrole films were synthesized in 'wet' and 'dry' conditions; pyrrole and thiophene copolymers were prepared at different potentials and bilayers were prepared by sequential deposition of polythiophene (PTh) and polypyrrole (PPy) films. The polymers were cycled between 2.0 V and 4.0 V in the lithium cells. The effects of disconnecting the electrodes from the cell on the behaviour of the polymers regarding doping and coulombic efficiency were also studied. The cycling performance of the 'wet' PPy is better than 'dry' PPy, bilayer PTh/PPy and copolymers. No mixed behaviour was observed for a bilayer where the inner layer was polythiophene and the outer layer was polypyrrol with a thickness PPy/Pth ratio equal to ten. The copolymer prepared at 3.9 V vs Li/Li^+ showed the higher energy capacity in $W\,h\,kg^{-1}$ calculated from the anodic charge.

1. Introduction

Conducting polymers such as polypyrrole, polyaniline and polythiophene have gained attention because of their application in devices such as batteries, electrochromic devices and supercapacitors [1–5]. These polymers have been employed in secondary batteries where lithium is used as negative electrode. However, the electrodes so far synthesized have several problems related to stability, adherence and conductivity, affecting the reversibililty of these electrodes which limits their employment in energy storage devices.

The characterization of electrochemically synthesized polypyrrole electrodes has been examined in the lithium perchlorate–propylene carbonate electrolyte by cyclic voltammetry, charge–discharge cycling, frequency response analysis and by vis–near i.r. absorption spectra [6]. The results show that these polymer electrodes behave satisfactorily in terms of kinetics of the electrochemical doping process, cyclability and the charge–discharge efficiency. However, their performance under high rates may be limited by the diffusion of the perchlorate counterion. The preliminary evaluation seems to indicate that polypyrrole may be more stable than other conducting polymers in organic electrolytes of interest for the development of rechargeable lithium batteries. On the other hand, the electroactivity and potential-dependent conductivity of polypyrrole films are strongly affected by the solvent and the solubility of the doping anions in the solvent [7].

The performance of polypyrrole (PPy) in lithium cells appears to depend strongly on the conditions of the electrosynthesis [8]. The samples obtained at high current densities have a markedly more porous surface morphology and are preferred for electrochemical applications. Also, it is well known that water added to the reaction medium exercises a favourable action on the synthesis of PPy as far as this morphology and related properties (e.g., conductivity) are concerned [9]. Lately, novel composite electrode structures have been prepared by single-step electropolymerization of polypyrrole onto a porous graphite fibre matrix by Coffey *et al.* [10]. They made batteries with a large fraction of the available charge which could be used over multiple cycles.

However, PPy has worse mechanical properties (toughness, adherence) than other polymers such as polythiophene (PTh) which, on the other hand, may be a prospective candidate as a positive electrode in lithium batteries. The lower price of the monomer, as well as the higher redox potential, are advantages in comparison with PPy. However, a lower stability of PTh fims during charge and discharge cycles have been noticed [11].

Polymer modified electrodes have been the subject of considerable interest. The combination of different materials may take the form of metal particulates in a polymer matrix [12, 13], metal/polymer/metal sandwiches [14], composites of one polymer within another [15] or bilayers of two segregated polymers [16]. In the case of composites, most studies have been aimed at combining the desirable properties of the two polymers. This has involved attempts to combine mechanical strength with electronic conductivity.

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In this paper we present a comparative study of the PPy, copolymers of pyrrole(Py)–thiophene(Th) and bilayers of PTh/PPy polymers in propylene carbonate $LiClO_4$ electrolyte. The purpose is to analyse the behaviour of the different polymers as positive electrodes in a lithium battery under cycling.

2. Experimental details

The electrolyte preparation, synthesis of the polymers and electrochemical characterization were performed in an Ar-filled glove box, thus avoiding contamination by oxygen and water. The base electrolyte, 0.5 M $LiClO_4$ /propylene carbonate (PC), was prepared and dried as in [17]. Polypyrrole (PPy) samples were grown on a Pt foil of 2 cm^2 geometrical area by electrolysis from a 0.5 M $LiClO_4$ solution in propylene carbonate containing 0.2 M pyrrole. Wet PPy (with 0.56 M H_2O added) was synthesized galvanostatically at 0.25 mA cm^{-2}. 'Dry' PPy was prepared potentiostatically at 3.8 V vs Li/Li^+. The thickness of the sample was calculated on the basis of the formula proposed by Diaz and Castillo [18], where 24 mC cm^{-2} corresponds to 0.1 μm. The electrosynthesis was carried out in a controlled atmosphere dry box using a four-electrode cell where the Pt substrate was in one compartment, two Li counter electrodes and the Li reference electrode were in the others. The same type of cell was used for the electrochemical characterization of the electrosynthesized PPy, copolymers (Py–Th) and bilayer (PTh/PPy) electrodes.

Electropolymerization of pyrrole and thiophene copolymers was carried out potentiostatically oxidizing pyrrole under diffusion limiting conditions at potentials where thiophene oxidation takes place [19]. The concentration of pyrrole was 2.0×10^{-3} M while that of thiophene was set at 0.1 M.

The polarization curves for the electropolymerization of pyrrole, thiophene and their mixture are shown in Fig. 1. The filled curve corresponds to the polymerization of pyrrole. It shows a limit current at potentials above 4.0 V vs Li/Li^+. The dotted curve corresponds to thiophene and the dashed curve to the mixture of pyrrole and thiophene. The copolymers were obtained at different potentials which are indicated on the corresponding curve, the values being 3.9 V, 4.0 V, 4.1 V, 4.2 V and 4.3 V.

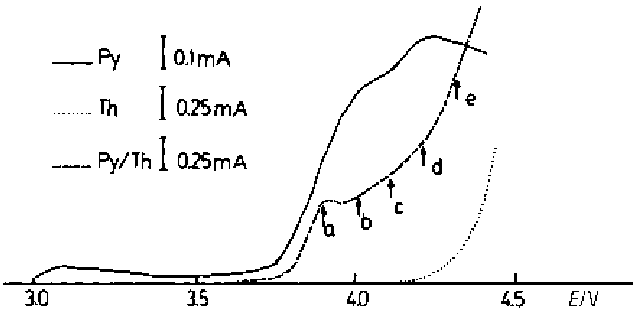

Fig. 1. *I/E* curves of the Pt electrodes in $LiClO_4$/PC solutions. Key: (—) pyrrole 2.0×10^{-3} M ; (·····) thiophene 0.1 M; (- - - -) mixture of pyrrole and thiophene.

Bilayers of polythiophene and polypyrrole were also prepared under potentiostatic conditions by sequential electrodeposition of inner and outer layer polymers. A thin film of PTh was prepared on platinum as the first layer from a 0.5 M $LiClO_4$ solution in propylene carbonate containing 0.2 M thiophene at constant potential of 4.4 V vs Li/Li^+. The thickness of this first layer (0.6 μm) was calculated from the charge involved in the polymerization process. The PTh polymer was washed in 0.5 M $LiClO_4$/PC and then placed in 0.002 M pyrrole/0.5 M $LiClO_4$/PC solution for synthesis of the second layer of PPy at 3.8 V vs Li/Li^+ (thickness 4.9 μm).

All polymers were treated as follows: undoping was performed in the same solution where polymerization took place at a slow sweep rate from the potential at open circuit up to 2.0 V vs Li/Li^+. The electrode was held at this potential for 60 min until an undoped level was achieved [17]. The electrode was then removed from the cell, washed in the dry 0.5 M $LiClO_4$/PC electrolyte and then placed in the cycling cell which contained 0.5 M $LiClO_4$/PC electrolyte. Before cycling the electrodes were potentiostatically held at 2.0 V for 30 min.

3. Results and discussion

The potentiodynamic behaviour of a freshly electrodeposited PPy layer, prepared in 'wet' conditions, is shown in Fig 2. The *E/I* curve (a) corresponds to the first discharge at a slow voltage scan rate in a polymerization solution. A sharp discharge peak is observed at 2.5 V. The PPy polymer was treated according to the procedure described in Section 2 (reduced in the polymerization solution from the open circuit potential to 2.0 V, washed and put in 0.5 M $LiClO_4$/PC solution and cycled between 2.0 V and

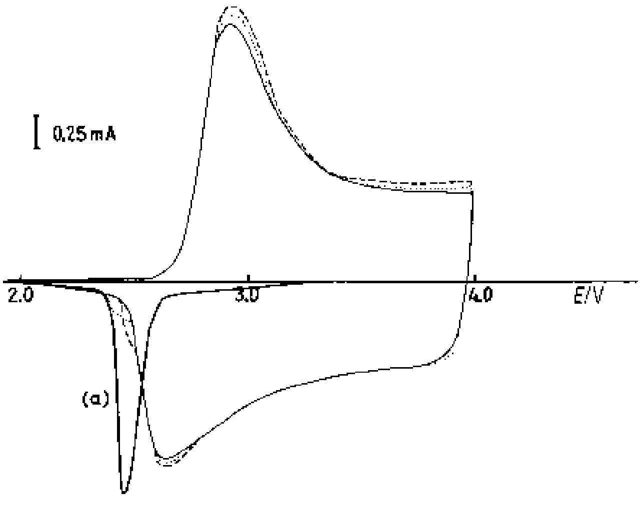

Fig. 2. Potentiodynamic discharge and cyclic voltammogram of polypyrrole (5 μm) prepared under 'wet' conditions. Curve (a): Potentiodynamic discharge in pyrrole– $LiClO_4$/PC solutions at 1 mV s^{-1} from the rest potential. Cycling in $LiClO_4$/PC solutions: (——) first cycle; (·····) 50th cycle; (- - - -) 400th cycle. Scan rate: 5 mV s^{-1}.

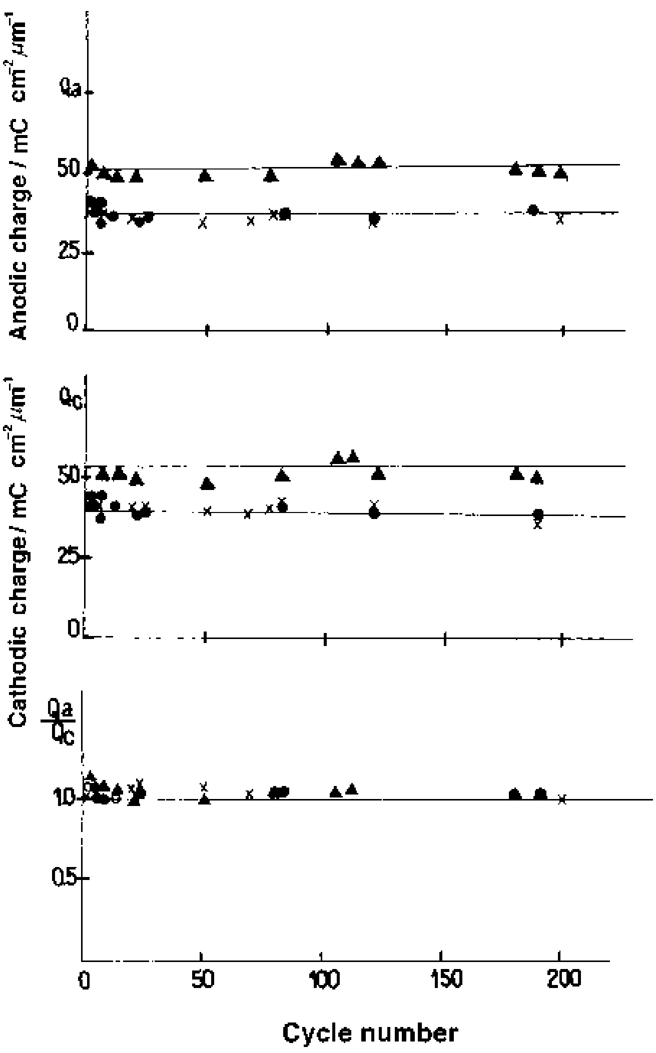

Fig. 3. Dependence of the anodic charge, Q_a, cathodic charge, Q_c, and Q_a/Q_c ratio with cycling of 'wet' PPy at different thicknesses: (▲) 1 μm, v = 10 mV s^{-1}, (●) 5 μm, v = 5 mV s^{-1}, (×) 10 μm, v = 1 mV s^{-1}.

4.0 V Li/Li$^+$). The figure clearly shows that the integrated charge under the reduction wave Q_c is similar to that under the oxidation wave, Q_a. This gives a coulombic efficiency, $\eta = Q_a/Q_c$, which approaches 100%.

The values of Q_a, Q_c and Q_a/Q_c as a function of cycle number for three PPy at different nominal thicknesses (1, 5 and 10 μm) are given in Fig. 3(a), (b) and (c), respectively. Other authors have reported that the charge values for the different polymers depend on the sweep rates and their thickness. These effects are due to the kinetics of the electrochemically doping process of PPy in the LiClO$_4$ which may be controlled by the diffusion of ClO$_4^-$ within the bulk of the polymer electrode [20]. Thicker polymers need slower sweep rates. On the other hand, the lower charge value of Q is obtained for PPy with 10 μm thickness. It has been reported that the higher level of doping is reached for films of around 1 μm thick for PPy galvanostatically prepared at 0.4 mA cm^{-2} [7]. The level of doping was calculated according to the following equation:

$$y = 2Q_d/(Q_{ed} - Q_d) \qquad (1)$$

where Q_{ed} is the electrodeposition charge (polymerization) and Q_d is the charge of the first discharge [21].

The 'wet' polymers of PPy were treated in the following way to study the charge capacity conditions. Following cycling, they were disconnected from the circuit and held outside the solution in the dry box. They were then replaced in the cell, connected to the control circuit and cycled between 2.0 and 4.0 V vs Li/Li$^+$. The procedure was repeated several times with all the polymers.

Figure 4 shows cycling behaviour for polymers of 5 μm submitted five times to the above described treatment. The polymers recovered their charge–discharge capacity in the first cycles and underwent a significant change in the cathodic charge after the fourth treatment (Fig. 5). Table 1 summarizes the voltammetric results for PPy electrodes: Q_a, Q_c, the coulombic efficiency, η, and the level of doping for the different charge–discharge cycles of the 'wet' polymers both newly prepared and those treated by disconnection of the circuit. The response of the electrodes to cycling in the charge–discharge processes as well as the recovery of the charge after disconnection from the cell is good. As previously shown in Fig 3, the higher charge level is reached with the 1 μm polymers. The coulombic efficiency is almost equal to 1 and the level of doping is 44% for 2000 cycles in PPy 1 μm thick and 35% for PPy 5 μm and 10 μm thick. The effect of disconnecting the electrodes from the cell on the behaviour of the polymers regarding doping and coulombic efficiency results in a decrease in the level of doping. This level is higher than 30% for polymers of 5 μm and 10 μm thickness

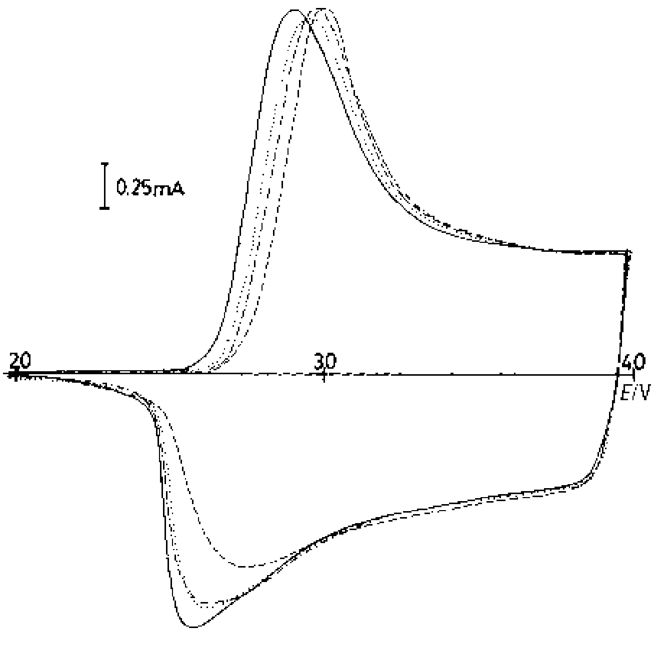

Fig. 4. Effect of disconnecting the electrodes from the cell: (——) without disconnecting; (·····) first treatment; (-·-·-) second treatment (- - - -) fourth treatment. Scan rate: 5 mV s^{-1}.

Table 1. "Wet" PPy electrodes in LICIO$_4$–PC solutions

Thickness /μm	*Sweep rate* /mV s^{-1}	*Cycle number*	*Anodic charge* Q_a/mC cm^{-2} μm^{-1}	*Cathodic charge* Q_c/mC cm^{-2} μm^{-1}	$\eta = \frac{Q_a}{Q_c}$	*Doping* /%
1	10	2	51.3	44.7	1.14	45
		180	50.2	48.0	1.05	50
		1090	47.3	46.2	1.02	48
		2000	48.8	43.4	1.12	44
5	5	2	38.5	35.6	1.08	35
		20	36.9	36.2	1.09	35
		190	37.6	35.4	1.06	35
	first treatment	1	38.1	35.6	1.07	36
		90	36.9	35.2	1.05	34
		500	35.4	35.5	1.00	35
	second treatment	1	38.0	35.6	1.06	35
		90	35.7	35.4	1.01	35
		330	35.0	34.9	1.00	35
		600	36.2	34.0	1.06	33
	third treatment	1	34.1	30.0	1.14	32
		30	33.4	33.0	1.01	32
		200	34.4	33.0	1.04	32
		460	34.6	32.7	1.06	32
	fourth treatment	50	34.3	32.0	1.07	31
10	1	20	37.2	35.4	1.05	35
		100	37.5	35.6	1.05	35
	first treatment	100	33.2	32.0	1.04	31
	third treatment	120	33.0	31.2	1.06	30
	fourth treatment	150	33.0	31.0	1.06	30
	fifth treatment	120	33.0	31.2	1.05	30

depending on the thickness. The coulombic efficiency remains at 100%.

Due to adherence problems of the polymers in films with thicknesses higher than 1 μm and taking into account that the PTh has a working potential higher than the PPy vs Li/Li$^+$, it was attempted to combine the PPy and PTh properties by preparing copolymers of pyrrole and thiophene. The potentiostatic method described earlier was used; the potentials chosen are those indicated in Fig. 1 and the preparation was performed in dry solutions following the procedures described in Section 2.

With the object of comparing the electrochemical behaviour of the conducting polymers of pyrrole and thiophene with that of PPy and taking into account that the properties of the conducting polymers depended on the preparation conditions [8], it was necessary to prepare 'dry' PPy in pyrrole solutions with

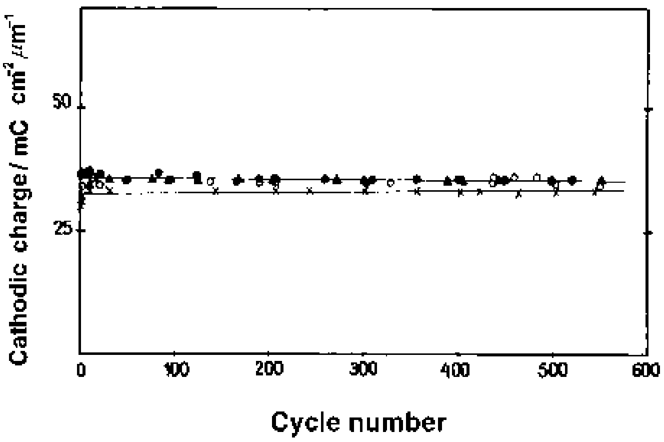

Fig. 5. Cathodic charge from cyclic voltammetry from Fig. 4 of 'wet' 5 μm PPy films as a function of the cycle number: (●) without disconnecting; (▲) first treatment; (○) second treatment; (×) fourth treatment. Scan rate: 5 mV s^{-1}. 0.5 M LiClO$_4$/PC.

a concentration equal to that used in the synthesis of copolymers, 0.002 M of pyrrole at a constant potential of 3.8 V.

Figure 6 shows the variation of the cathodic charge with cycling for a PPy 'dry' polymer of 4.7 μm thickness. The corresponding voltammogram is shown on the upper right angle of the figure. The charge values involved in the oxidation-reduction process and the efficiency values, η, at different cycle numbers are given in Table 2. The values of Q_a, Q_c and η are similar to those found in the 'wet' polymers. The anodic charge is slightly higher than the cathodic but the behaviour with cycling and with disconnection from the cell reveals that the response to the cycling of the 'wet' polymer is better than that of the 'dry' polymer (Table 1).

The pyrrole and thiophene copolymers were prepared at the potential vs Li/Li$^+$ indicated in Fig. 1 (3.9, 4.0, 4.1, 4.2 and 4.3 V). Cyclic voltammograms of the copolymers in a propylenecarbonate solution containing 0.5 M LiClO$_4$ are shown in Fig. 7. An anodic peak and a rounded cathodic maximum appear at different potentials. The I/E response shows that the polymers are not mixtures of PPy and PTh because, in that case, two couples of anodic/cathodic peak currents should have appeared at different potentials due to the redox reactions of PPy and PTh. The polymer obtained at a potential 3.9 V vs Li/Li$^+$ shows a voltammetric behaviour similar to that of the polypyrrole, whereas that prepared at 4.2 V is similar to PTh [19].

Table 3 shows the values of the rest potentials in LiClO$_4$/PC solutions and of the anodic peak potentials for copolymers prepared at different potentials. The values corresponding to polymers of pyrrole prepared under potentiostatic and galvanostatic conditions are also included for comparison. The rest potentials and the anodic peaks are again systematically changed from those of PPy ($E_r = 3.7$ V vs Li/Li$^+$ to those of PTh ($E_r = 4.4$ V). The value of the anodic peak potential also varies from 2.8 V (PPy polymer) to 3.95 V (copolymers). The copolymers were cycled between 2.0 V and 4.0 V in the lithium cells like the 'wet' and 'dry' PPy polymers. The

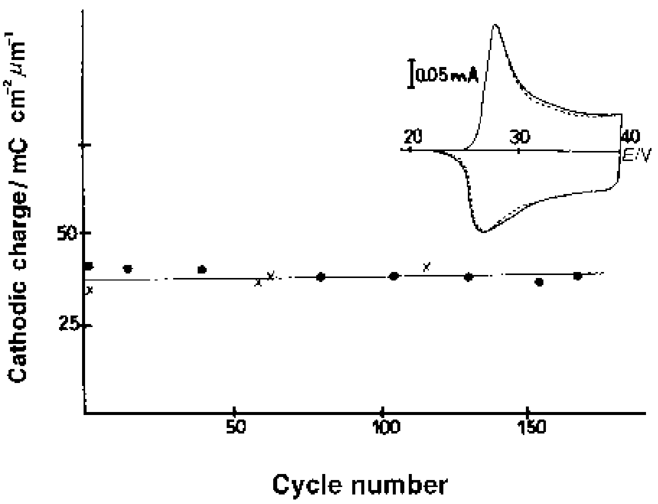

Fig. 6. Cyclic behaviour of 'dry' polypyrrole (4.7 μm) prepared under dry conditions at 3.8 V vs Li/Li$^+$. Cyclic voltammogram: (——) first cycle; (- - - -) 80th cycle. Cathodic charge: (●) without disconnecting of cell; (×) first treatment. Scan rate: 5 mV s^{-1}.

Table 2. "Dry" PPy electrodes in LiClO$_4$–PC solutions

Thickness /μm	*Sweep rate* /mV s^{-1}	*Cycle number*	*Anodic charge* Q_a/mC cm^{-2} μm^{-1}	*Cathodic charge* Q_c/mC cm^{-2} μm^{-1}	$\eta = \frac{Q_a}{Q_c}$	Doping /%
1.02	10	120	41.8	40.6	1.03	37
	first treatment	1000	39.1	38.2	1.02	41
			38.7	36.2	1.07	35
4.7	5	1	48.7	40.8	1.19	41
		15	43.7	40.6	1.07	40
		40	43.4	40.2	1.08	40
		80	41.6	39.7	1.05	40
		105	39.5	36.8	1.07	36
		131	40.8	37.3	1.09	37
		154	38.6	34.8	1.11	34
	first treatment	2	44.6	35.0	1.27	34
		59	44.1	36.9	1.19	36

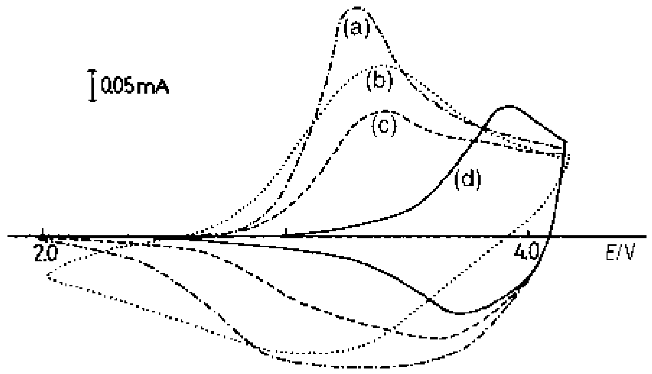

Fig. 7. Cyclic voltammograms of the copolymers in $LiClO_4$/PC solution. Preparation potential of copolymers: (a) 3.9, (b) 4.0, (c) 4.1 and (d) 4.3 V vs Li/Li^+.

Table 3. Pyrrole and thiophene polymer

Copolymer	*Thickness /μm*	*Preparation potential /V*	*Rest potential /V*	*Peak anodic potential /V*
a	3.9	3.9	3.84	3.38
b	5.4	4.0	3.89	3.17
c	5.0	4.1	3.83	3.42
d	4.7	4.2	3.78	3.95
e	5.1	4.3	3.94	3.98
"dry" PPy	1.0	3.8	3.69	2.81
	4.7	3.8	3.65	2.82
PTh/PPy	0.6	4.4		
	5.0	3.8	3.70	2.85

anodic and cathodic charges of the polymer layers were evaluated from the cyclic voltammograms by integrating the anodic and cathodic currents. Figure 8 shows the variation of Q_a, Q_c and Q_a/Q_c with the number of cycles for the polymer synthesized at different potentials.

The charge of copolymers (a) shows a slight increase with increasing cycle number. The copolymer (b) shows a slight decrease in the charge with cycle number. Both of them show high charge value. On the other hand, the behaviour of copolymers (c) and (d) is worse than (a) and (b) considering that the values of the charges are lower and decrease with cycling.

Other polymers of pyrrole and thiophene were prepared employing bilayers of PTh/PPy and their behaviour in the lithium cell were studied. The voltammetric response for a bilayer of 0.6 μm of PTh and 5 μm of PPy is indicated in Fig. 9. A good current-potential response is obtained. No mixed behaviour is observed for a bilayer where the inner layer is polythiophene and the outer layer is polypyrrole with a thickness almost tenfold higher as has been reported by Hillman *et al.* [16]. They studied PTh/PPy bilayer polymers in acetonitrile with polypyrrole (outer) and polythiophene (inner) electrodes, with a similar PTh/PPy mole ratio and showed that PPy response is superimposed on the positive half of the PTh response and the negative end of the PTh response is suppresed. The authors explained that the PTh films were not compact and coherent and, consequently, PPy monomers could diffuse into the PTh and polymerize to give a PTh–PPy composite. In our

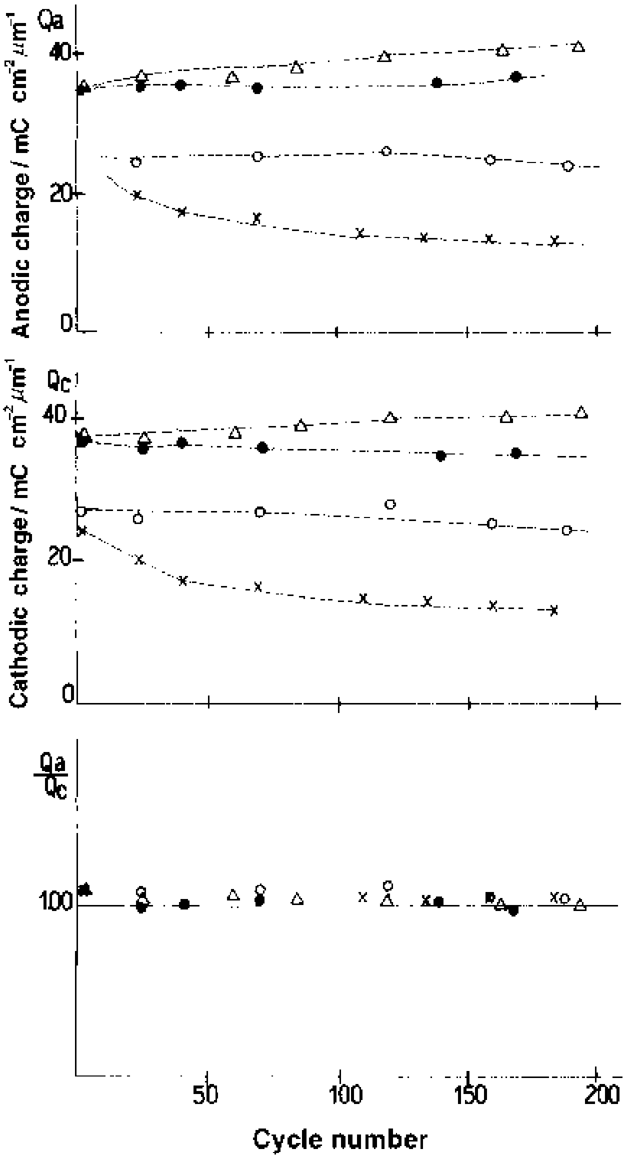

Fig. 8. Dependence of the anodic charge, cathodic charge and Q_a/Q_c ratio with cycling of copolymers prepared at (△) 3.9, (●) 4.1, (○) 4.2 and (×) 4.3 V.

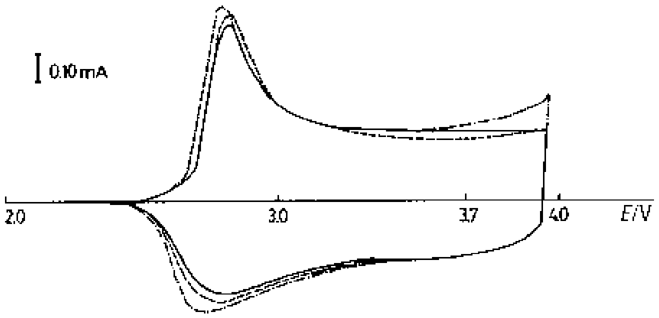

Fig. 9. Repetitive cyclic voltammetry of PTh/PPy bilayer in $LiClO_4$/PC solution. $v = 5\,mV\,s^{-1}$. PTh 0.6 μm thickness, PPy 5 μm thickness. (——) first cycle; (- - - -) 40th cycle; (-·-·-) 170th cycle.

case we can detect that effect. If the 'dry' PPy voltammogram is superimposed on a PTh/PPy voltammogram, the response is exactly the same.

The 'dry' PPy polymers, copolymers and bilayers of pyrrole and thiophene were disconnected from the cell to study the charge capacity. The results obtained for the cycling of these electrodes are given in Table 4. The charge values and the doping level of the copolymers (a) and (b) are similar to 'dry' PPy polymers. They also show a good response to the open circuit treatment.

The comparative study of the conductor polymer behaviour using the charge values and doping level is limited by the potential interval for cycling. In the case of copolymer cycling above 4.2 V vs Li/Li^+ results in higher coulombic capacities but causes a gradual irreversible oxidation during cycling as found in the cycling of polythiophene polymers [11]. Therefore, the performance of the different polymers was compared using the specific capacity.

The specific capacity in $Ah\,kg^{-1}$ was calculated as follows. The values of the total anodic charge of

Table 4. Pyrrole and thiophene polymers

Copolymer		*Cycle number*	*Anodic charge* $Q_a/mC\ cm^{-2}\ \mu m^{-1}$	*Cathodic charge* $Q_c/mC\ cm^{-2}\ \mu m^{-1}$	$\eta = \frac{Q_a}{Q_c}$	Doping /%
a (3.9 V)		23	37.0	35.4	1.04	35
		86	39.0	37.5	1.04	37
		205	40.5	39.5	1.02	39
	first treatment	1	45.7	42.4	1.08	42
		91	45.6	42.3	1.08	43
b (4.0 V)		2	37.0	35.0	1.05	34
		25	36.0	36.0	1.00	35
		43	35.0	35.5	1.00	35
		103	35.0	36.0	1.00	35
	first treatment	4	35.0	32.1	1.09	30
		43	33.5	32.6	1.01	31
		72	32.3	31.0	1.04	29
c (4.1 V)		23	26.0	24.5	1.06	23
		70	27.0	25.0	1.08	24
		117	28.0	25.5	1.10	24
		195	24.0	23.0	1.04	22
	first treatment	24	21.6	19.7	1.10	18
		150	19.1	17.0	1.12	15
d (4.2 V)		23	19.5	19.5	1.00	18
		38	17.5	17.0	1.03	16
		137	13.6	13.0	1.05	12
	first treatment	1	15.8	13.4	1.18	12
		116	13.4	13.7	1.02	12
PPy/PTh bilayer		20	40.8	37.0	1.10	37
		140	43.0	40.1	1.07	39
	first treatment	15	36.6	35.0	1.05	35
		120	38.0	33.9	1.12	35

Table 5. Properties of pyrrole and thiophene polymers as electrode material for lithium batteries

Polymer 5 *μm thickness*	*Anodic charge* /mC cm^{-2}	*Specific capacity* /A h kg^{-1}	*Working potential* /V	*Energy density* /W h kg^{-1}
"wet" PPy	188	34.8	2.60	90.5
"dry" PPy	193	35.7	2.73	97
Copoly (a)	198	36.7	3.12	114
Copoly (b)	182	33.7	3.25	109
Copoly (c)	115	21.3	3.65	78
Copoly (d)	68	12.6	3.75	47
PTh / PPy	183	33.9	2.83	97

those polymers with a thickness of around 5 μm were taken. The charge in mC cm^{-2} was normalized at this value and the value of the reference density was taken [8]. Table 5 lists the values of the specific capacity, as well as the working potential, at different potentials vs Li/Li$^+$ for the polymer in the lithium cells prepared by using different methods : (i) constant current ('wet' PPy), (ii) potentiostatic deposition: 'dry' PPy, copolymers and bilayer polymers. The energy density in W h kg^{-1} can also be estimated from these values. It can be observed that copolymers (a) have a specific energy 28% higher than the dry and wet pyrrole polymers and a bilayer of PTh/PPY.

4. Conclusion

The performance of pyrrole and thiophene polymers has been studied in a lithium cell with lithium perchlorate–propylene carbonate electrolyte using voltammetric measurements. Different polymers have been prepared: 'wet' PPy, 'dry' PPy, Py–Th copolymers and PTh/PPy bilayer polymers.

The charge–discharge process was analysed through the anodic charge, cathodic charge and doping level obtained from the voltammograms. The effect of disconnecting the electrodes from the cell and the subsequent charge recuperation was also studied. The 'wet' PPy showed the best behaviour.

From the charge values, the specific capacity and energy density were calculated for all the polymers. The pyrrole–thiophene copolymer prepared at 3.9 V vs Li/Li$^+$ gave a higher value than the 'dry' and 'wet' polypyrrole.

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