SCHEMES FOR THE USE OF CONDUCTING POLYMERS AS ACTIVE MATERIALS IN ELECTROCHEMICAL SUPERCAPACITORS

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ABSTRACT

The development of a novel conducting polymer based system for use in electrochemical capacitors is described. This system utilizes a new conducting polymer, poly-3-(4-fluorophenyl)-thiophene (PFPT), that can be reversibly n- and p-doped to high charge density. The electrochemical n-dopability of this material can be further improved by cycling in acetonitrile solution that contains a new electrolyte, tetramethylammonium trifluoromethanesulfonate ($Me_4NCF_3SO_3$). We discuss these improvements in n-dopability in terms of potential electronic and steric influences. We believe that the substituent fluorophenyl group does not communicate with the polythiophene backbone through resonance, and conclude that the ability to n-dope PFPT to high charge density may occur as a result of electron transfer reactions from the conducting polymer backbone into the substituent. This new system for electrochemical capacitors provides the best achievable performance from conducting polymers and generates high energy and power densities that are comparable with noble metal oxide systems, potentially at a fraction of the cost.

INTRODUCTION

A number of authors have described the potential application of conducting polymers as active materials in electrochemical capacitors [1-5]. Conducting polymers are advantageous in this application because, in a similar way to noble metal oxide electrodes, charge is stored through the volume of the material. This leads to higher charge densities (up to 500 C/g) than can be achieved by surface charging at activated carbon electrodes. It is anticipated that conducting polymer electrodes can be manufactured relatively cheaply, and are therefore potentially better suited to commercial applications, such as electric vehicles, than noble metal oxide based electrodes. Conducting polymers store charge in a manner that is analogous to doping processes at semiconductors. Electrons are either removed from (p-doping) or added to (n-doping) the conjugated π-systems of the organic polymer, and overall charge neutrality is maintained by incorporation of anions or cations respectively, into the polymer. These doping processes can be performed chemically or electrochemically, and the area is well reviewed [6,7]. Because no electron transfer reaction takes place, and in most cases nor do any phase transformations, the impedances which are associated with doping of conducting polymers can be small, and these are most often attributed to the rate limiting transport of counter ions through the micro- and nano-structure of the polymeric material [8]. Such low impedances make conducting polymers suitable materials for high power applications.

At the 182nd Meeting of The Electrochemical Society (Toronto, Fall 1992), we discussed two schemes by which conducting polymers can be used in electrochemical capacitors. In the Type I scheme, the same p-dopable conducting polymer (e.g. polypyrrole, polyaniline, polythiophene) is used at both electrodes and previously reported conducting polymer based electrochemical capacitors have been fabricated according to this scheme [3,4]. When the Type I capacitor is charged, one of the polymer electrodes is in its fully p-doped state, while the other is in its insulating, undoped state. The cell voltage is typically about 1 V. As the capacitor is discharged the p-doped film dedopes and the undoped film dopes, until both films are half-doped when the cell voltage is zero. In our Type II scheme, two different p-dopable conducting polymers are used, one at each electrode. The two materials are chosen by virtue of the different electrochemical potential ranges over which they dope and dedope (e.g. polypyrrole with polyaniline or polythiophene). In this way the voltage (up to about 1.5 V) and charge density of the device are increased over Type I, and the resulting energy density is much improved.

In this paper we describe a third scheme for electrochemical capacitors which improves further on Type II. In the Type III electrochemical capacitor, the electrode active material is a conducting polymer which can be both n- and p-doped. Thus, when the capacitor is charged, one of the polymer electrodes is in its p-doped state and the other is in its n-doped state. As the capacitor is discharged, both films dedope and both are in their undoped, insulating state when the cell voltage reaches zero. The cell voltage of a charged type III capacitor (about 3 V) is higher than either Type I or II, and we will show how this translates into a further improvement in energy density. The Type III capacitor has two added advantages over Types I and II. Firstly, when Type I and II capacitors are charged, one of the electrode films is in its undoped, insulating state and this is likely to significantly diminish the instantaneous power density of the device. This situation is not experienced in the Type III system. Secondly the characteristics of discharge of a Type III device are similar to that of a battery in that all the charge is released at high voltage (typically between 2 V and 3 V). In this way there is no redundant charge in the device that is being stored at too low a voltage to be useful to the particular application (e.g. to drive the motor in an electric vehicle).

Because of the similarity between the performance of our Type III capacitor and that of a battery, a number of authors have reported conducting polymer batteries that are of the same basic concept as the Type III capacitor [9-12]. With the exception of the polythiophene battery of Kaneto et al [9], all these devices employ polyacetylene as the active conducting polymer material. This conducting polymer is not suitable as the electrode material in an electrochemical capacitor, because very high impedances are associated with the electrochemical doping of polyacetylene [13], and this results in a large hysteresis in the voltammetric peaks both for p- [14] and n- [13] doping. Hence the power density and the energy cycle efficiency of a polyacetylene-based Type III capacitor are expected to be too low for practical applications. Polythiophene is a much more suitable material for electrochemical capacitors because much more reversible n- doping can be achieved [15-18]. However the ability to n-dope polythiophene diminishes rapidly with polymer films thicker than 1 µm. For energy storage applications, thicker films than 1 µm are needed, and this was recognized in the polythiophene battery paper of Kaneto [9]. The presence of a phenyl group in the 3-position of the thiophene monomer has been reported to improve the ability to n-dope the resulting polymer over polythiophene [19] Therefore we sought to investigate this phenomenon more closely and synthesized other 3-arylthiophenes in order to achieve the best n-doping. In this way we hoped to identify a suitable conducting polymer material for a Type III capacitor.

EXPERIMENTAL

Of key importance to the fabrication of conducting polymer electrodes for electrochemical capacitors, is to allow easy electrolyte access to the maximum volume of polymer material. To this aim, a planar film electrode is not well suited because electrolyte access to parts of the film becomes more difficult as the film is thickened. At very thick polymer films (>30 µm) this is expected to lead to excessively high impedances associated with charging and discharging, and as a result diminish accessible power densities. We have developed a new technique for electrode fabrication, which permits much easier electrolyte access to a large volume of conducting polymer. The conducting polymer is electrodeposited, by galvanostatic oxidation of the monomer, onto a lightweight fibrous carbon paper support. In this way the polymer forms into sheaths (currently the optimum thickness of the sheath is 10 µm) around the individual carbon fibers (8 µm). Hence, the mass of polymer per geometric square cm can be increased, by increasing the thickness of the carbon paper, without changing the maximum distance of ionic penetration through the polymer, required for complete polymer doping (10 µm). We found that different polymer materials grew onto the carbon papers in different ways. This can be seen in the scanning electron micrographs in Figure 1, of carbon paper electrodes with polypyrrole and polybithiophene. These pictures were taken at electrodes which had been broken after polymer growth to reveal the inner carbon fibers.

Electrochemical experiments were performed in either a standard 3-electrode cell or a 5-electrode cell that included two adjacent working electrodes and two counter electrodes. This latter design permitted polymer growth, single electrode cyclic voltammetry, potentiostatic setting of specific doping levels, and constant current discharge between the two working electrodes (i.e. in a capacitor configuration), all without the need to alter the cell assembly between stages. The working electrodes were fabricated from 75 µm thick carbon paper (Toray - approx. 75% free volume), cut into a spade shape to ensure that a fixed area of electrode is exposed to the solution Note, any quotes of geometric current, charge and energy densities in this paper refer to the area of carbon paper, not the real area of the surface of the carbon fibers. This carbon paper is uniform in its geometric weight distribution, which allows us to calculate the mass of electrodeposited polymer by weighing and subtracting for the carbon. Before weighing any electrode, the conducting polymer was potentiostatically undoped to remove any dopant ions, and washed to remove solvent and electrolyte. Counter electrodes were made from 750 µm thick Toray carbon paper Working and counter carbon electrodes were connected to platinum wire with silver loaded epoxy and an outer coating of regular epoxy above the liquid level in the cell. The reference electrode was a standard Ag/Ag^+ electrode for non aqueous systems, comprising of a silver wire immersed in the respective working solution, with silver nitrate added to the level of 0.02 mol/dm^3 This reference compartment was separated from the working solution by a porous glass plug. All electrode potentials quoted in this paper are with respect to the Ag/Ag$^+$ electrode.

All electrochemical experiments were performed in a controlled argon atmosphere glove box. Cyclic voltammograms were iR corrected by the PAR 273 potentiostat. Acetonitrile (Sure-Seal, <50 ppm water) was used as solvent throughout. Three tetraalkylammonium salts were used in this work. Et_4NBF_4 and Bu_4NPF_6 were recrystallized four times from acetone and ethanol-water respectively. $Me_4NCF_3SO_3$ is a new electrolyte chosen specifically for this work. $Me_4NCF_3SO_3$ was synthesized by titrating an aqueous solution of tetramethylammonium hydroxide with trifluoromethanesulfonic acid until the pH just passes below 7. The water and small amount of excess acid were removed by evaporation. The crude salt was first dissolved in acetone and the residue filtered off, followed by four recrystallizations from acetone-hexane. The melting point of the white solid was 383-384°C and elemental analysis supported the calculated empirical content of the material: element-{calc.||obsvd.}: C-{26.91% ||26.87%}; H-{5.42% ||5.13%}; N-{6.28% ||6.17%}; F-{25.53% ||24.1%}; S-{14.3% ||14.55%}. The aryl substituted thiophenes were prepared according to literature procedures *via* a nickel-catalyzed coupling of 3-bromothiophene with the appropriate aryl magnesium bromide [20]. The aryl substituted monomers were typically white solids that were purified by sublimation, and all displayed satisfactory physical and spectroscopic properties according to previous reports [19,21,22]. Pyrrole was purified by filtering through a column of activated alumina, and bithiophene was used as received. All the chemicals listed above were purchased from Aldrich in the purest available grade.

RESULTS

The structures, names and acronyms for the monomers and polymers that we have investigated are described in Table 1. For an ideal electrode in a Type III capacitor, the active material should n-dope to the same high charge density as it p-dopes, at a relatively thick film. As all the polythiophenes we tested p-dope to similar levels, we estimated that a film of polymer grown onto the 75 μm carbon paper at a growth charge of about 5 C/cm^2, would provide sufficient geometric energy density for an electrochemical capacitor, provided that the resulting polymer n-dedopes to the same charge density that it p-dedopes. We specify dedoping charges here, rather than doping charges, because in the Type III capacitor, both electrodes are dedoping during discharge, and therefore it is the dedoping charges that define the energy output of the device. As a gauge of the unsatisfactory n-doping of polythiophene (PT), a film that was grown to an oxidation charge of 7.2 C/cm^2, showed no n-doping whatsoever, when cycled to -2.4 V at 50 mV/s in 1 mol/dm^3 Bu_4NPF_6 in acetonitrile. We therefore performed a series of experiments on polymers of the different 3-arylthiophenes, as cited in Table 1, in the hope of improving on the n-doping of PT. These experiments were performed in 1 mol/dm^3 Et_4NBF_4 in acetonitrile.

The cycling of poly-3-phenylthiophene (PPT), confirmed the report by Sato et al. [19], that this material exhibits improved n-doping over PT. However, PPT was still unable to n-dope to the levels we required. A film of PPT grown at 7.2 C/cm^2 displayed a ratio of n-dedoping charge to p-dedoping charge of 21%. Interestingly, both in Sato's work and ours, the potentials for n- and p-doping appeared not to change greatly from PT to PPT. This would appear to contradict Sato's suggestion that the improvement in n-doping occurs as a result of the electron withdrawing effect of the phenyl group's π

system on that of the polythiophene backbone. This would be expected to shift the potentials for both p- and n-doping to more positive potentials. The simplest alternative explanation is that steric influences are the cause. In this way the phenyl group might push adjacent polymer chains apart allowing easier access through the polymer for dopant cations. We therefore chose to test poly-3-(*p*-tolylthiophene) (PTT) and poly-3-(4-*t*-butylphenyl)-thiophene (PBPT), to see if the addition of further sterically demanding groups would continue the improvement. The testing of these two materials is particularly useful in this regard as the effect of the added alkyl groups can be assumed to have negligible effect on the electronic properties of the conducting backbone. There was little difference in the n-doping and dedoping behavior of either PTT or PBPT, with respect to PPT.

The two other 3-arylthiophenes we tested were chosen for possible electronic effects. Sterically, poly-3-(4-fluorophenyl)-thiophene (PFPT) and poly-3-(4-trifluoromethylphenyl)-thiophene (PTFMPT) can be expected to be very similar to PPT and PTT respectively, as the physical size of -F is similar to -H. Both -F and $-CF_3$ are strongly electron withdrawing inductively, although -F is electron donating through resonance [23]. The electrochemical behavior of PFPT and PTFMPT were significantly different, both with respect to each other, and with respect to PPT. PTFMPT displayed a positive shift in the peak potentials for both n- and p- doping of about 200 mV over PTT. However this material also exhibited a very significant degree of "charge-trapping". Charge-trapping refers to a proportion of the doping charge (n-, p- or both) that is not released during the subsequent dedoping sweep, but remains 'trapped' in the material as the potential is scanned through the insulating region of the voltammogram. This phenomenon is observed because as the material undopes, regions of doped material become isolated from the rest of the electrode by regions of undoped, insulating polymer. Charge-trapping has been reported and discussed for polythiophene and other n-dopable conducting polymer electrodes [17,24]. In our experiments, we observed some degree of charge-trapping in all the polythiophene-based materials we tested, however none were at the same degree as PTFMPT. We have discussed charge trapping in our systems in more detail elsewhere [25].

Success in our work came with the testing of PFPT. The peak potentials for p- and n- doping/dedoping of PFPT were almost identical to those for PPT, as indeed was the charge associated with p-doping (approximately 1 electron per 4 monomers). However the charge associated with n-doping was significantly improved. This is demonstrated very clearly in Figure 2, which shows cyclic voltammograms for films of PT, PPT and PFPT which p-dope to the same degree. This result, in conjunction with the lack of further improvement in PTT and PBPT, seems to suggest that while the improvements evident in Figure 2 appear to be due to electronic factors, these are not simply through an extension of the polymer's conjugated system to include the substituent aryl groups. The degree to which the π-system of the aryl substituent communicates with the polymer backbone can be estimated by calculating the value of the dihedral angle between them using molecular mechanics. Our calculations for the dihedral angle in the monomers (PCModel */Serena Software inc./*, Chem 3D+ */Cambridge Scientific Computing inc./*, and CAChe */Cache Scientific inc./*) give a value of 25-30°, and this should allow some degree of π electronic communication. However, these calculations only account for intramolecular steric interactions in a single monomer. Much greater inter- and intramolecular forces are likely to influence the aryl group within a solid polymer film. Our preliminary MM2 calculations (CAChe) indicate that the average dihedral angle in a polymer film may be higher than 60°. This would explain why the voltammetric peak positions for p- and n-doping of PT, PPT and PFPT are very similar, but not why the charges associated with n-doping are so different.

We propose that the improvements in n-doping we have observed are seen as a result of electron transfer reaction from the polythiophene backbone into the substituent aryl group. According to this theory, PFPT is better than PPT because it is easier to reduce fluorophenyl than phenyl. Some amount of charge could still be transferred to the phenyl groups in PPT over the potential range where the polythiophene backbone n-dopes, and this would explain the improvement in PPT over PT. If this theory is correct then it could also explain the high degree of charge-trapping observed with PTFMPT. Assuming the reduction potential for trifluoromethylphenyl (TFMP) is more positive than that for fluorophenyl, then charge-trapping at PTFMPT would occur because a large proportion of the reduced TFMP groups remain as such when the polythiophene backbone becomes undoped and insulating. In this way the reduced TFMP groups are electronically isolated from the current collector when the voltage is swept passed their oxidation potential, so they can only oxidize when the polythiophene backbone becomes conducting again, in the early stages of p-doping. In possible support of the theory described above, the group of Roncali have reported the n-doping of polythiophenes where different aryl groups were attached to the thiophene monomer at the 3-position, via a -(C_2H_4)-O-(CH_2)- ether linkage [26]. The saturated linking group completely isolates the aryl group electronically from the polythiophene backbone, and yet these authors report improved n-doping when fluorophenyl was the attached group, relative to that when the group was phenyl. It should be noted that the authors propose that structural and/or morphological differences explain their observations, however there is no supporting evidence for this. Further experiments are needed in support of either of these views.

At a growth charge of 7.2 C/cm^2, the ratio of the n-dedoping and p-dedoping charges, for a film of PFPT in 1 mol/dm^3 Et_4NBF_4 in acetonitrile, is 60%. Thus for electrochemical capacitor applications, still further improvements were desirable. This was achieved by optimizing the electrolyte in which PFPT is cycled. Thick films of PFPT n-doped to a higher charge density in tetraethylammonium solutions than in tetrabutylammonium solutions of the same ionic strength. The logical step was therefore to use a tetramethylammonium salt, as alkali metal salts were found to be unsuitable for n-doping polythiophenes both by ourselves and other workers [17,27]. (There is one report of PPT n-doping in lithium perchlorate in acetonitrile [28], however we were unable to reproduce this result.) The difficulty with tetramethylammonium salts was that there were no reports of one that was highly soluble in acetonitrile and electrochemically stable through the potential range over which polythiophenes p- and n-dope. Although there are many reports of other tetraalkylammonium trifluoromethanesulfonates, there were none in relation to the tetramethylammonium salt. As these salts were known to be stable and had low melting points (and hence high solubilities in polar solvents), we synthesized $Me_4NCF_3SO_3$ ourselves, according to the protocol described in the experimental section. Using PFPT in a 1 mol/dm^3 solution of this material, in acetonitrile (conductivity 0.025 S/cm), we achieved the degree of n-doping we required. Indeed, the proportion of n dedoping charge to p dedoping charge in this system, remained over 100%, even at a growth charge of 20 C/cm^2. A comparison of the cyclic voltammograms for the same film of PFPT in 1 mol/dm^3 solutions of Bu_4NPF_6 and $Me_4NCF_3SO_3$ in acetonitrile, are presented in Figure 3 to illustrate the effect of cation size. To date, the best reported system for the n-doping of a polythiophene based material, was PPT in 1 mol/dm^3 Et_4NBF_4, described by Sato et al. [19] Figure 4 describes the two stages of improvement we have achieved over this system, by comparing the ratio of n-dedoping to p-dedoping charges for PPT in 1 mol/dm^3 Et_4NBF_4, PFPT in 1 mol/dm^3 Et_4NBF_4 and PFPT in 1 mol/dm^3 $Me_4NCF_3SO_3$, as a function of polymer growth charge.

We performed constant current discharge experiments between two conducting polymer electrodes, in order to calculate the energy densities corresponding to our three schemes for electrochemical capacitors. For the Type I capacitor we tested two electrodes containing polypyrrole (PPy); for the Type II capacitor we tested one electrode of PPy with one of polybithiophene (PBT); for the Type III capacitor we tested two electrodes of PFPT. To aide comparison, all experiments were performed in 1 mol/dm^3 $Me_4NCF_3SO_3$ in acetonitrile. The films of PPy and PFPT were polymerized at a growth charge of 20 C/cm^2; the growth charge corresponding to the film of PBT was 15 C/cm^2, as this produced a film which p-doped to approximately the same charge as the PPy electrode. In our Type II experiment, we chose to electropolymerize bithiophene rather than thiophene, because the high potentials required for oxidation of the latter have been reported to overoxidize the resulting polymer [17,18]. The discharge curves for the three experiments are presented in Figure 5, for a constant current of 200 µA. The area under these curves represents the energy of discharge (as $E = i\int V dt$ in a constant current experiment). The improvements from Type I to Type II to Type III are evident. This is confirmed in Table 2, which displays the values of charge and energy density calculated from these results.

CONCLUSIONS

We have been able to show how the n-dopability of polythiophene can be improved by aryl substitution of the thiophene monomer in the 3-position. This improvement is the most significant when the aryl substituent is *p*-fluorophenyl. The reasons for the improvement remain unclear. Although steric factors may be are involved, these cannot fully explain the different electrochemical characteristics we have reported. Based on our results, we propose that the n-doping charge density at PFPT is higher than at PPT because the fluorophenyl substituent in PFPT is more easily reduced, by electron transfer from the polythiophene backbone, than the phenyl substituent in PPT. In this way, the polymer material is acting like a redox polymer, with localized redox active sites attached to the polymer backbone. The ability to reversibly n-dope PFPT at thick films (>10 µm) to the same charge density as p-doping (approx. 1 electron per 4 monomers) is an impressive improvement on previous reports. For electrochemical capacitors, 39 Wh/kg of active material is a excellent value, in view of the DOE goal for these devices in application to electric vehicles (5 Wh/kg of device) [29]. Of the previously described all-conducting-polymer batteries and capacitors, only the polyacetylene and polythiophene batteries improve on this energy density [9-12]. Both of these systems require that the polymer films are very thin, and the polyacetylene battery also suffers from poor reversibility and cycle life. We have previously shown that the anticipated power density for a device made from our system of PFPT/carbon paper in 1 mol/dm^3 $Me_4NCF_3SO_3$ in acetonitrile, is also significantly in excess of current DOE goals [30].

In terms of the combination of energy density, power density and materials cost, conducting polymers represent the most attractive technology described so far for the active material in electrochemical capacitors. If satisfactory cycle life and efficiency can be demonstrated with these materials, then their potential for commercial use may be realized. We look forward to performing further experiments on power density, cycle life and cycle efficiency, on other new materials, as well as those described in this paper

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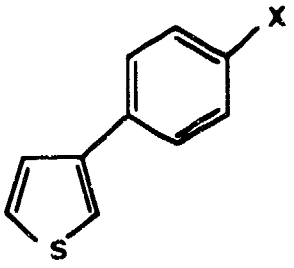
TABLES AND FIGURES



Substituent X	Monomer Name	Polymer Acronym
-	pyrrole	PPy
-	thiophene	PT
H	bithiophene	PBT
CH_3	3-phenylthiophene	PPT
$C(CH_3)_3$	3-(*p*-tolylthiophene)	PTT
F	3-(4-*t*-butylphenyl)-thiophene	PBPT
CF_3	3-(4-fluorophenyl)-thiophene	PFPT
	3-(4-trifluoromethylphenyl)-thiophene	PTFMPT

TABLE 1: The different monomers, and the acronyms used for the corresponding polymers investigated in this work, including those based on *p*-substituted 3-phenylthiophene (general molecular structure shown).

Scheme	Voltage	Charge Density		Energy Density		
	V	[a] C/cm^2	[b] C/g	[a] J/cm^2	[b] J/g	[b] Wh/kg
I	1.0	1.2	86	0.56	41	11
II	1.5	2.2	120	1.9	100	27
III	3.1	1.3	52	3.5	140	39

TABLE 2: Charge and energy densities obtained in experiments on the three schemes for the application of conducting polymers to electrochemical capacitors.

[a] Charge and energy densities calculated per geometric cm^2 of the carbon paper electrodes.

[b] Charge and energy densities calculated per gram of active material on both electrodes in the capacitor configuration.

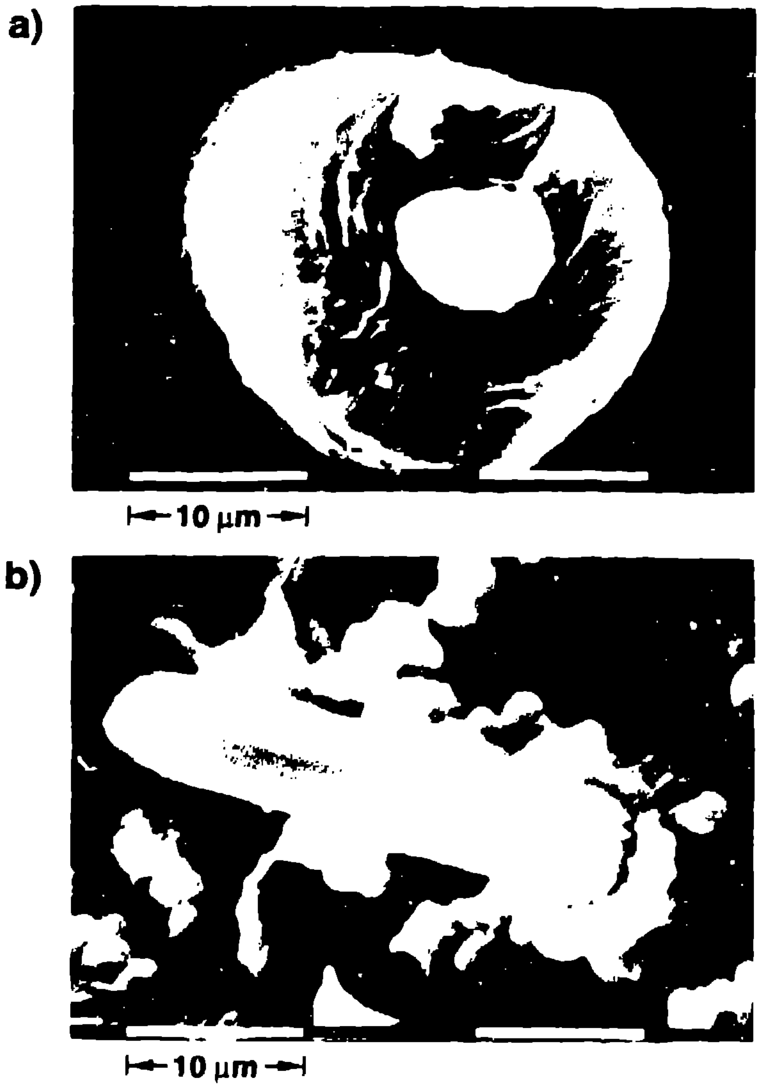


FIGURE 1: Scanning electron micrographs at the broken edge of a 75 μm thick carbon paper electrode (inner fibrils), which is the substrate to electrodeposited layers (outer sheaths) of **a)** polypyrrole and **b)** polybithiophene. The conducting polymer films were grown at constant current onto the carbon paper out of 0.1 mol/dm^3 monomer, 1 mol/dm^3 $Me_4NCF_3SO_3$ in acetonitrile. The polymer growth charges were 20 C/cm^2 for the polypyrrole electrode and 15 C/cm^2 for the polybithiophene electrode.

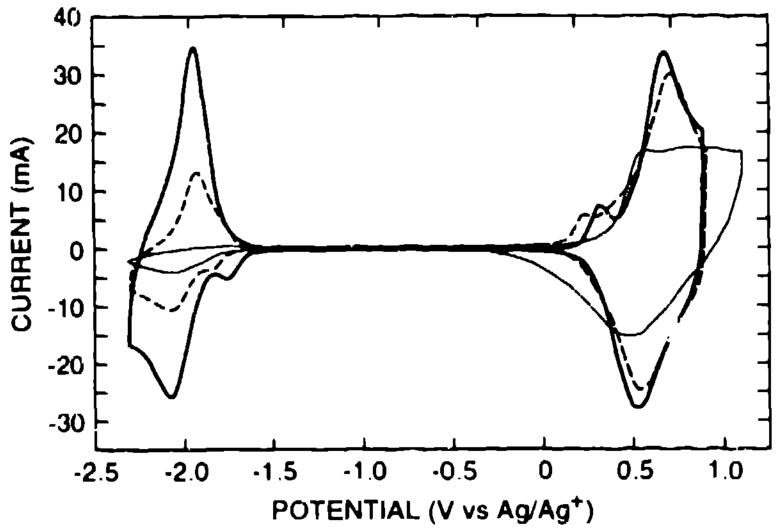


FIGURE 2: Cyclic voltammograms at 25 mV/s for films of PT (thin full line), PPT (dashed line) and PFPT (thick full line), in 1 mol/dm^3 Et_4NBF_4 in acetonitrile. The polymer films were grown galvanostatically onto 1.0 cm^2 x 75 µm carbon paper at 2 mA for 3,000 seconds (PT) or 2,000 seconds (PPT and PFPT), out of 0.1 mol/dm^3 monomer, 1 mol/dm^3 Et_4NBF_4 in acetonitrile.

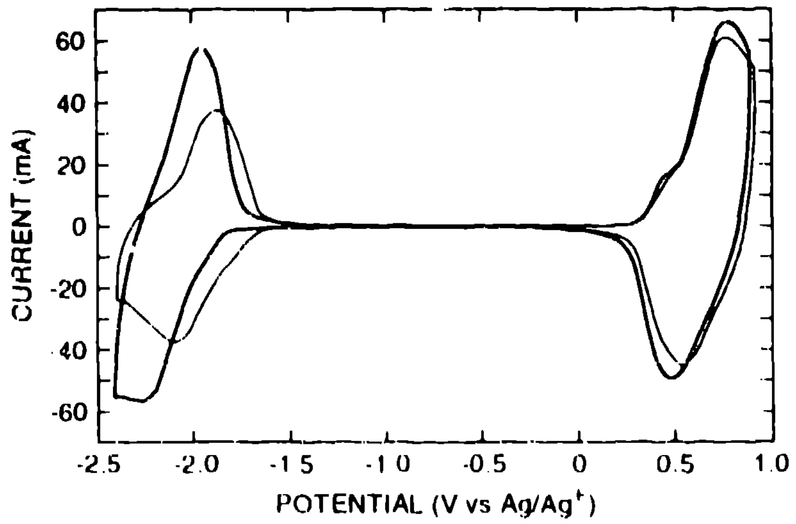


FIGURE 3: Cyclic voltammograms at 25 mV/s for a film of PFPT in 1.0 mol/dm^3 $Me_4NCF_3SO_3$ in acetonitrile (thick line) and in 1.0 mol/dm^3 Bu_4NPF_6 in acetonitrile (thin line). The PFPT film was grown galvanostatically onto 1.0 cm^2 x 75 µm carbon paper at 2 mA for 4,000 seconds out of a solution of 0.1 mol/dm^3 FPT, 1 mol/dm^3 $Me_4NCF_3SO_3$ in acetonitrile.

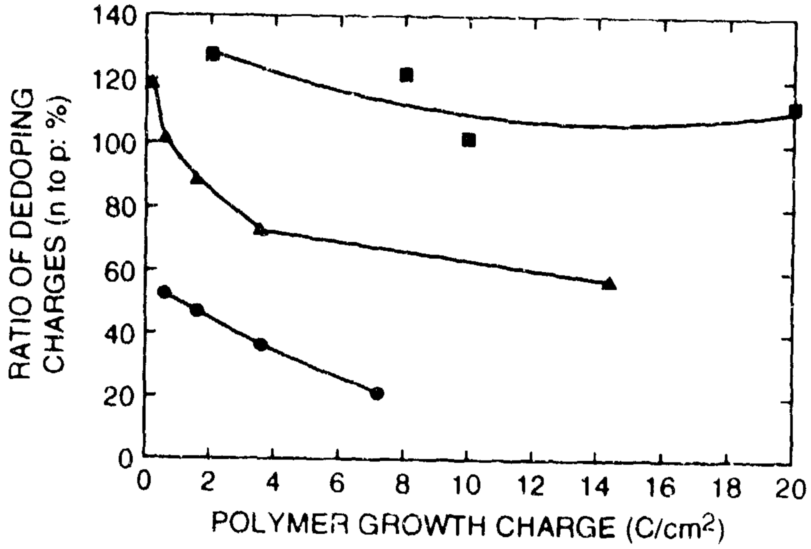


FIGURE 4: The improvements in n-dopability, measured as the ratio of n-dedoping charge to p-dedoping charge in a 50 mV/s cyclic voltammogram, for different polymer thicknesses of (i) PPT in 1 mol/dm^3 Et_4NBF_4 in acetonitrile (circles); (ii) PFPT in 1 mol/dm^3 Et_4NBF_4 in acetonitrile (triangles); and (iii) PFPT in 1 mol/dm^3 $Me_4NCF_3SO_3$ in acetonitrile (squares); In each of the three cases, at a given polymer growth charge, the p-dedoping charges are approximately the same.

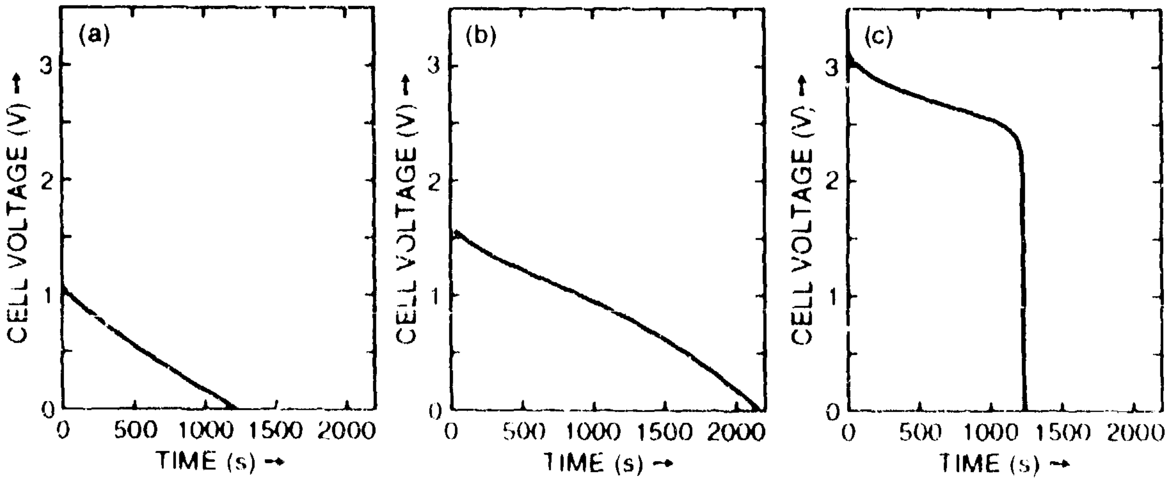


FIGURE 5: Results from the experiments to determine the energy densities of Type I, II and III capacitors. Each figure shows the decay in the cell voltage, as a discharge current of 200 μA is passed between two polymer electrodes in a solution of 1 mol/dm^3 $Me_4NCF_3SO_3$ in acetonitrile. **a)** Type I - PPy/PPy; **b)** Type II - PBT/PPy; **c)** Type III - PFPT/PFPT.