

Conducting polymers as active materials in electrochemical capacitors

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Abstract

Electronically conducting polymers represent an interesting class of materials for use in electrochemical capacitors thanks to the combination of high capacitive energy density and low materials cost. Three generalized types of electrochemical capacitors can be constructed using conducting polymers as active material, and in the third of these, which utilizes conducting polymers that can be both n- and p-doped, energy densities of up to 39 Wh per kg of active material on both electrodes have been demonstrated. This energy density is obtained using poly-3-(4-fluorophenyl)-thiophene (PFPT) in an electrolyte of 1 M tetramethylammonium trifluoromethanesulfonate (TMATFMS) in acetonitrile. This unique system exhibits reversible n- and p-doping to high charge density in relatively thick films of the active polymer and a cell voltage exceeding 3 V in the fully charged state. Impedance data for both n- and p-doped PFPT suggest that high power densities can be obtained in electrochemical capacitors based on this active conducting polymer.

Introduction

Over the past ten years, electronically conducting polymers have received significant attention thanks, in part, to the potential application of these materials in battery cathodes [1–4], in electrochromic displays [5, 6], in electronic devices [7], and in a number of other systems of industrial interest [8–11]. A number of reviews on relevant properties of conducting polymers have been published [12–14]. Another potential application recently suggested for conducting polymers is that of the electrode-active material in electrochemical capacitors, which are high power, energy storage devices now receiving growing attention [15–17]. An electrochemical capacitor is very much the same as a battery except that the nature of charge storage in the electrode active material is capacitive, i.e., the charge and discharge processes involve only translation of ionic and electronic charges through electronically or ionically conducting domains, respectively. Energy densities of electrochemical capacitors are much higher than those of ordinary capacitors, but typically lower than those of advanced batteries (<10 Wh/kg). However, compared with batteries, high power densities (>500 W/kg) and longer cycle life (>10⁵ cycles) have been either demonstrated or projected. These latter advantages over batteries are achievable because no rate-determining and life-limiting phase transformations take place at the electrode/electrolyte interface. The most eagerly anticipated application of electrochemical capacitors is as a power storage device in

an electric vehicle (EV), operating in parallel with the EV battery. The EV capacitor will be discharged at a high rate during acceleration and hill climbing, and recharged when traveling at constant speed and during deceleration, either from the battery or by regenerative braking. By removing the need for pulses of peak power from the EV battery, it is expected that the battery size will be reduced and battery life extended.

Conducting polymers can be synthesized either chemically or electrochemically, and in the majority of cases this is done by oxidation of the relevant monomer in solution. Once formed, these polymers can exist in either two or three general states. As-formed polymers tend to be in the oxidized or 'p-doped' state, in which the polymer backbone is positively charged and has high electronic conductivity, normally in the range of 1–100 S/cm. Reducing the p-doped polymer generates the 'undoped' state. The latter is usually insulating, or semi-insulating, depending on the degree of completion of the undoping process. For a limited number of polymers, primarily polyacetylene [18–20], poly-p-phenylene [21, 22] and polythiophenes [22, 23], electrochemical reduction of the undoped polymer is also possible in a suitable stable environment, leading to the reduced, 'n-doped' state, which is also associated with significant electronic conductivity [24]. For a polymer that can be both p- and n-doped electrochemically, the separation in the onset electrode potentials for p- and for n-doping is a measure of the optical band-gap of the polymer [25]. Although the analogy to semiconductors is not perfect, the process of electrooxidation or electroreduction of the non-conducting state of the polymer generates mobile electronic charge carriers in the material, and this is why these charging processes can be referred to as chemical doping. Charge neutrality always has to be maintained, and therefore the injection of an electronic charge during doping has to be accompanied by appropriate exchange of an ionic charge with the electrolyte solution. This requires, in turn, that a conducting polymer film of high charge/discharge activity has good electronic and good ionic conductivities. The latter requirement is usually fulfilled by a network of electrolyte-filled micropores and/or nanopores within the active film of the conducting polymer. The mobility of the 'free' electronic charges in conducting polymers is smaller than in semiconductor materials, because of the absence of good long range order. This is the reason for the less-than-metallic conductivity observed in such materials, in spite of the large concentration of electronic charges in their doped state. However, the electronic conductivity typically obtained for the 'doped' state of a conducting polymer (1–100 S/cm) is significantly higher than the ionic conductivity of highly conducting liquid electrolytes. Therefore, the electronic conductivity would not generally limit the dynamics of the charge/discharge process in a film of a conducting polymer, unless exhaustive dedoping occurs.

In the doping processes at conducting polymer electrodes, charging takes place through the volume of the active film. Doping levels as high as one electron per two monomeric building blocks can be achieved in the case of polyaniline (even higher levels can be achieved in a carefully-selected environment [26]) and this corresponds to a charge density of 500 C/g. In the context of active materials for electrochemical capacitors, charging through the volume of the material is an advantage of conducting polymers over high surface area carbon. In the latter case, the charging process is confined to the solid/electrolyte interface. The other technology currently being pursued for the active material in electrochemical capacitors is noble metal oxide electrodes, predominantly RuO_2 and mixed oxides where RuO_2 is the major component [15]. Charging in such electrodes has been reported to take place through the volume of the material and, as a result, the charge and energy densities observed are comparable with or even slightly higher than those obtained at conducting polymer electrodes [15].

However, conducting polymers also possess the advantage of potentially low materials cost. It can be anticipated that electrodes of relatively simple conducting polymers, such as polyaniline, polypyrrole and polythiophene, can be fabricated at a cost comparable with that of carbon capacitor electrodes, and much lower than that of noble metal oxide electrodes. It is the combination of low materials cost and high energy density that makes conducting polymers attractive potential active materials for use in electrochemical capacitors.

Some question may arise as to whether electrochemical energy storage devices based on conducting polymers, noble metal oxides or redox polymers, should be referred to as 'electrochemical capacitors', as done here, or, rather as 'batteries'. This issue has been addressed before in some detail by Conway [17]. Indeed, devices based on conducting polymers have been referred to in the past as either electrochemical capacitors [15, 17, 27–33] or as batteries [34–41]. Our three criteria for preferring the electrochemical capacitor terminology have been: (i) the nature of the fundamental process of charge/discharge in these electrochemical systems; (ii) the combination of typical energy and power density levels achieved in these systems, and (iii) the phase angle of the interfacial impedance at a frequency around 0.1 Hz. Further discussion of these criteria is provided in the Appendix.

Classes of capacitors based on conducting polymer active materials

The mechanism of electrochemical doping of a conducting polymer film is described schematically for p-doping in Fig. 1(a) and for n-doping in Fig. 1(b). As shown in Fig. 1(a), electrochemical p-doping of conducting polymers takes place by abstraction of electrons from the polymer backbone through the external circuit and incorporation of an anion from solution into the polymer film to counter balance the positive electronic charge. The mechanism of electrochemical n-doping of conducting polymers

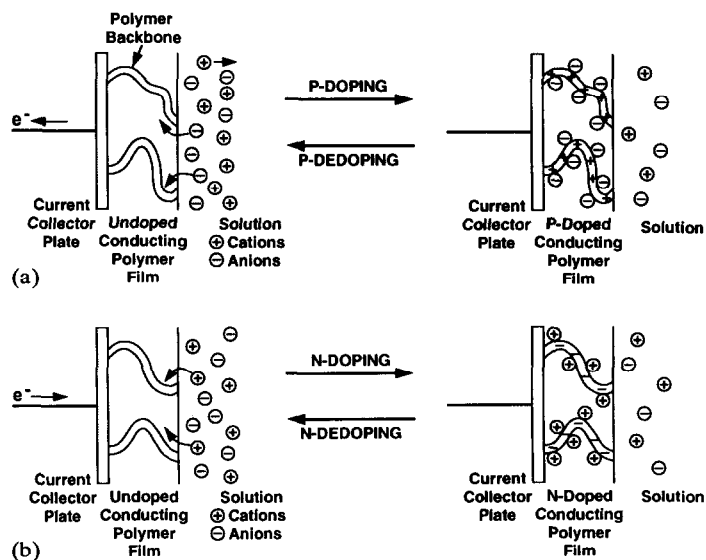


Fig. 1. A schematic representation of the charging and discharging processes at conducting polymer electrodes associated with (a) p-doping and (b) n-doping.

proceeds by the reverse of this mechanism as evident in Fig. 1(b). Electrons are transported onto the polymer backbone by the external circuit, and cations enter the polymer from the solution phase in order to maintain overall charge neutrality. Most conducting polymers can be p-doped and undoped, and these processes generally take place at electrode potentials that are accessible in aqueous solutions. Conversely, only a limited number of conducting polymers can be reversibly n-doped, virtually all at highly reducing electrode potentials which require cathodically stable and relatively pure non-aqueous systems. For these reasons most workers have concentrated on the p-doping of stable conducting polymers such as polypyrrole [42, 43] and polyaniline [44, 45]. However, reliance on p-doping/undoping alone in a single type of active material typically limits the overall voltage window of the device to about 1 V. For this reason, we have pursued other configurations of capacitors based on conducting polymer active materials, which would provide an increased voltage window, and hence an increased energy density.

Figures 2 to 4 show schematically electrochemical characteristics for the three types of capacitor systems considered in this paper. For each type of system considered, a generalized, schematic voltammogram is presented for a single electrode containing the conducting polymer active material (Figs. 2(a), 3(a) and 4(a)), together with a corresponding voltage decay curve expected at constant discharge current in a capacitor made with two such active electrodes (Figs. 2(b), 3(b) and 4(b)). The schematic forms of the voltammogram shown in these Figs. are characteristic for conducting polymer

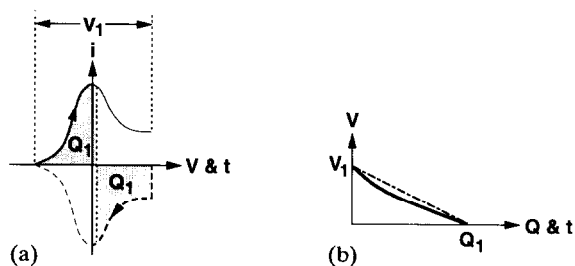


Fig. 2. Generic characteristics expected for the Type I electrochemical capacitor; a symmetric system using a p-dopable conducting polymer on each electrode of the capacitor. (a) The generic voltammogram for the active material. (b) Solid line describes the predicted voltage decay under constant-current discharge for a capacitor using materials with the generic voltammogram shown in part (a); the dashed line gives, for comparison, the decay curve expected for the same device if the differential capacitance were constant.

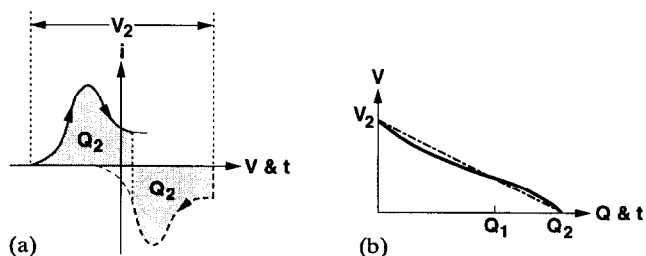


Fig. 3. Generic characteristics expected for the Type II electrochemical capacitor; an unsymmetric system based on two different p-dopable conducting polymers; (a) and (b) show generic voltammograms for single electrodes and capacitor discharge curves, respectively.

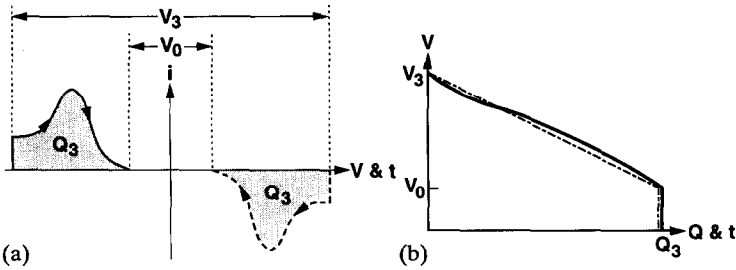


Fig. 4. Generic characteristics expected for the Type III electrochemical capacitor; a symmetric system based on a conducting polymer which can be both p- and n-doped. Parts (a) and (b) show generic voltammograms for single electrodes and capacitor discharge curves, respectively.

materials which undergo conversion from an undoped to a doped state. Typically, such an electrochemical conversion is associated with a peaked, rather than featureless voltammogram. Low capacitive currents are observed in the undoped region and high capacitive currents in the doped region, i.e., the differential capacitance of the material is potential dependent. This general form of the voltammogram has been analyzed by a number of authors [46, 47]. During the discharge of a capacitor fabricated with two conducting polymer electrodes, the potential of each electrode shifts from the highest positive, or highest negative value, to a final potential set by the condition of zero discharge current and zero voltage (as shown by the arrows on the voltammograms in parts (a) Figs. 2–4). The voltage decay at constant current, shown in parts (b) of Figs. 2–4, was reconstructed in each case from the generic voltammogram. The nonlinearity of the discharge characteristic (bold curve in parts (b) of Figs. 2–4), is a result of the potential dependence of the differential capacitance. The energy, E , released during discharge of the capacitor, can be calculated from the area under the actual discharge curve, according to: $E = I \int V dt$, where I is the constant discharge current and V the voltage measured across the capacitor.

In the Type I electrochemical capacitor (Fig. 2), the active components of the two electrodes comprise of two identical, p-dopable conducting polymer films. When the capacitor is fully charged, one of the films will be in the undoped form, the other will be in the fully doped form and the cell voltage is V_1 (typically 1 V). Upon discharge, the undoped film oxidizes (becomes doped: thick full line, Fig. 2(a)) while the doped film reduces (dedopes: thick dashed line, Fig. 2(a)), until both are half-doped and the cell voltage is zero. Hence, the charge released on discharge, Q_1 , is only one half of the full doping charge. The conducting polymer-based electrochemical capacitors described previously by other laboratories [17, 27–31, 33b,d,e], are all fabricated according to the Type I scheme.

Figure 3 shows the basis for the improvement in energy density obtained in Type II capacitor configurations. In this scheme, two different p-dopable conducting polymers are used as the active materials on the two electrodes. These polymers are selected by virtue of the difference in potential ranges over which they become doped, as evident in the cyclic voltammograms, Fig. 3(a). This results in an increase of the voltage of the fully charged capacitor to V_2 (typically 1.5 V), and also allows a greater proportion of the total doping charge, Q_2 , to be released on discharge. The resulting increase in energy density over a Type I capacitor is reflected by the larger area under the cell voltage decay curve, Fig. 3(b).

The scaling of the energy of an ideal capacitor with V^2 ($E = 1/2CV^2$) explains the drive to increase further the voltage of the device. In the Type III capacitor described schematically in Fig. 4, cell voltages of more than 3 V can be achieved. The conducting polymer used in the Type III capacitor can be both n- and p-doped. When the capacitor is charged, one polymer film is fully p-doped and the other is fully n-doped. As a result, the initial cell voltage is increased further to V_3 (Fig. 4b), and the full doping charge, Q_3 , is released on discharge. When the cell is fully discharged, both polymer films are returned to their undoped state. The generic Type III capacitor has two further advantages over Types I and II. Firstly, the instantaneous power density on discharge should be greater, because both electrodes are in a doped, conducting state when the capacitor is fully charged. In contrast, in Types I and II one of the polymer films is in the undoped, semi-insulating state when the capacitor is charged and this could introduce a higher resistance into the fully charged device. Secondly, the Type III capacitor is advantageous because all the charge is released at relatively high cell voltages, and, hence, there will be no redundant charge stored at voltages too low to be useful, say to drive the motor of an electric vehicle.

Experimental

Experiments aimed at evaluating the energy density of active, charged conducting polymer materials were performed in an electrochemical cell of the design described in Fig. 5. The electrode assembly, consisting of a reference electrode, two working electrodes and two counter electrodes, was designed so the polymer films could be grown at constant current (passed between a working and a counter electrode), an initial doping level could be subsequently set potentiostatically in each working electrode, and the complete assembly could be transferred between growing, washing and cycling

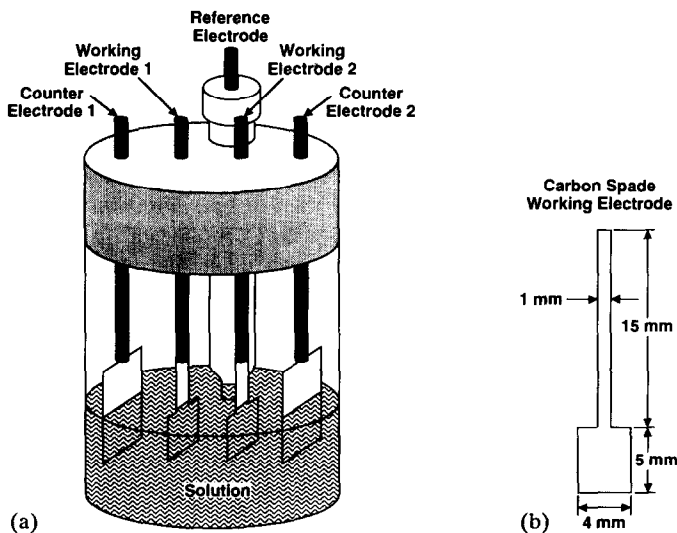


Fig. 5. (a) The electrochemical cell configuration used for testing the electrochemical characteristics of different conducting polymer materials electrodeposited on carbon paper. (b) The dimensions of the 3 mil ($75 \mu\text{m}$) thick carbon paper spade working electrodes.

solutions. Once the films were grown on the two working electrodes and the initial states of each active film had been set, the working electrodes were connected in a capacitor (two-electrode) mode to be charged and discharged galvanostatically.

The working electrodes were fabricated from 3 mil (75 μm) thick carbon paper into the spade shape shown in Fig. 5(b), allowing 0.20 cm^2 of carbon paper to be exposed to the working solution. The porous carbon paper electrodes were chosen to enable the deposition of a large volume of polymer per unit geometric area of electrode without necessitating the formation of a very thick polymer film which might reduce accessible power densities. The counter electrodes in voltammetric experiments were made of thicker carbon paper. Working and counter carbon paper electrodes were connected to platinum wire (above the liquid level in the cell) employing silver-loaded epoxy, with an outer coat of regular epoxy. The reference electrode was made up of a silver wire immersed in the working solution, with silver nitrate added to the level of 0.02 M. The reference compartment was separated from the working solution by a porous glass plug.

Impedance experiments were performed in a standard three-electrode cell configuration using a Solartron 1250 frequency response analyzer in conjunction with a Solartron 1286 electrochemical interface. Impedance spectra were recorded in the frequency range 10 kHz down to 0.1 Hz with an a.c. voltage amplitude of 20 mV.

Nonaqueous, acetonitrile solutions (< 50 ppm H_2O) were used, and all experiments were performed in a controlled atmosphere glove box. A new electrolyte was used in this work, tetramethylammonium trifluoromethanesulfonate (TMATFMS), and the reason for this choice is described later in the section 'type III capacitor' page 99. TMATFMS was synthesized by titrating an aqueous solution of tetramethylammonium hydroxide with 2 M trifluoromethanesulfonic acid until the pH just passes through 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. This new salt was found to be particularly effective in the case of our Type III system, as explained in the section of Type III capacitor, page xx. However, to enable the most direct comparison between all types of capacitors tested, solutions of TMATFMS in acetonitrile were employed in film growth and film cycling experiments for all three schemes. Tetraethylammonium tetrafluoroborate (Et_4NBF_4) was recrystallized four times from acetone and tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) was recrystallized four times from ethanol/water. For experiments with the Type III capacitors, the aryl-substituted thiophenes were synthesized by a Grignard coupling reaction of 3-bromothiophene with the respective aryl magnesium chloride compound [48, 49]. Bithiophene was used as received and pyrrole was cleaned of oligomers by filtering through a column of activated alumina. All the chemicals listed above were purchased from Aldrich in the purest available grade.

Results and discussion

Type I capacitor

Polypyrrole was used as the active material for the Type I capacitor experiment. Active films were grown from 0.1 M pyrrole, 1 M TMATFMS in acetonitrile at 1 mA for 4000 s. A relatively dense sleeve of polypyrrole, approximately 10 μm thick, formed on the carbon fibers as evident in the scanning electron (SEM) micrograph of a broken edge of the carbon paper electrode in Fig. 6. The films were washed in dry acetonitrile

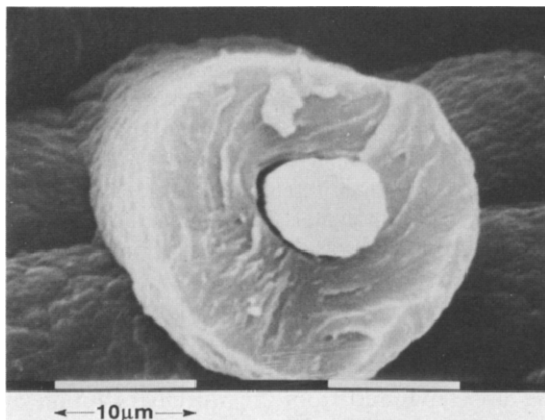
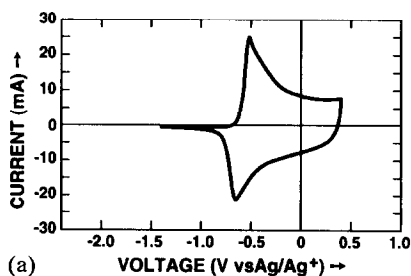
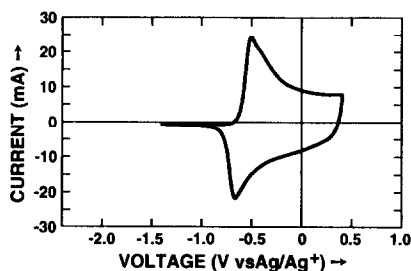
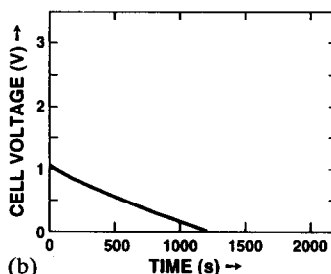


Fig. 6. Scanning electron micrograph of a polypyrrole film electrodeposited onto a carbon fiber as viewed at a broken edge of the polypyrrole/carbon paper electrode.



(a)



(b)

Fig. 7. Experimental results for a Type I electrochemical capacitor based on two electrodes of polypyrrole/carbon paper. (a) Cyclic voltammograms of the two polypyrrole films at 20 mV/s (solution iR compensated). (b) Voltage-time curve recorded during 200 μA discharge between the two polypyrrole/carbon paper electrodes. The carbon paper electrode is 75 μm thick and has a cross-sectional area of 0.2 cm^2 .

and transferred to a solution of 1 M TMAFMMS in acetonitrile. Cyclic voltammograms were recorded for the two polymer films and these are shown in Fig. 7(a). Subsequently, one film was potentiostatically undoped, the other doped, and then a constant current of 200 μA was passed between the two polymer electrodes operating in a capacitor discharge mode. The decay in voltage measured between the two electrodes as a function of time during discharge is presented in Fig. 7(b). From this Fig. values of

charge density and energy density were calculated per unit mass of capacitor active material (i.e., per unit mass of active material in a pair of working electrodes). The numbers obtained for the Type I capacitor are shown in Table 1, together with the values for Types II and III.

While the figure of 11 Wh/kg, obtained for the polypyrrole-based Type I system, is satisfactory, it is anticipated that the energy density per kg of a complete device would not represent a major improvement over the values already reported for high surface area carbon-based electrochemical supercapacitors (currently reported up to 2 Wh/kg [16, 50, 51]). In this aim, capacitors of Types II and III are significantly more attractive.

Type II capacitor

The two polymers employed in our Type II capacitor experiment were polypyrrole and polythiophene. The polypyrrole film was again grown from 0.1 M pyrrole, 1 M TMAFMS, in acetonitrile at 1 mA for 4000 seconds. The polythiophene film was grown out of 0.1 M bithiophene, 1 M TMAFMS in acetonitrile at 1 mA for 3000 s. Bithiophene was chosen as the growth monomer because the oxidation potential of thiophene is very high positive and this has been reported to lead to overoxidation of the growing polymer film [52]. The morphology of the polythiophene film was very different from that of the polypyrrole film. A loose particulate morphology was observed with clusters of particles evident on the surface of the carbon paper, and only a relatively thin sheath of polymer formed directly on the carbon fibers, as shown in the SEM micrograph of a broken edge of the carbon paper electrode in Fig. 8. The difference in the voltage ranges of high capacitance between the two polymers can be seen in the cyclic voltammograms in Fig. 9(a). Subsequent to the voltammetric experiment, the polypyrrole film was undoped, the polythiophene film doped, and then the constant current discharge experiment, at 200 μ A, was performed in a two-electrode mode. The voltage decay measured during this discharge can be seen in Fig. 9(b), and the results for charge and energy density obtained from Fig. 9(b) are presented in Table 1.

The improvement in energy density of the Type II capacitor over Type I is evident, and actually follows closely the improvement in energy of factor 2.25 predicted for an improvement in voltage of the charged capacitor of factor 1.5. Like the Type I system, Type II has the advantage of employing simple conducting polymers, that can be synthesized from inexpensive, commercially-available monomers. Furthermore, an

TABLE 1

Charge and energy density obtained in experiments on the three schemes we have proposed for the application of conducting polymers to electrochemical capacitors

Scheme type	Voltage (V)	Charge density		Energy density		
		(C/cm ²) ^a	(C/g) ^b	(J/cm ²) ^a	(J/g) ^b	(W h/kg) ^b
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

^aCharge and energy densities calculated per geometric cm² of the carbon paper electrodes.

^bCharge and energy densities calculated per gram of active material on both electrodes in the capacitor configuration. This does not therefore include the mass of the carbon paper.

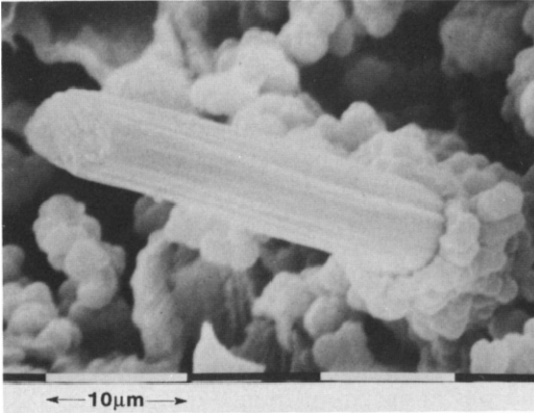


Fig. 8. Scanning electron micrograph at the broken edge of the polythiophene/carbon paper electrode used in the Type II capacitor experiment.

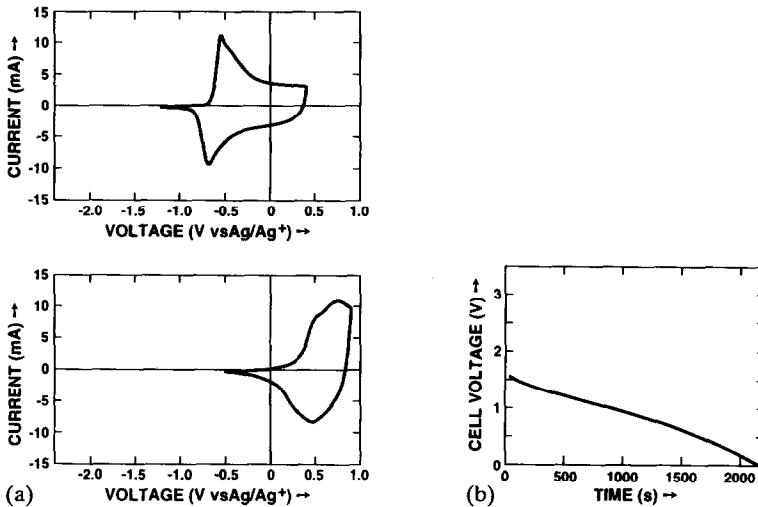
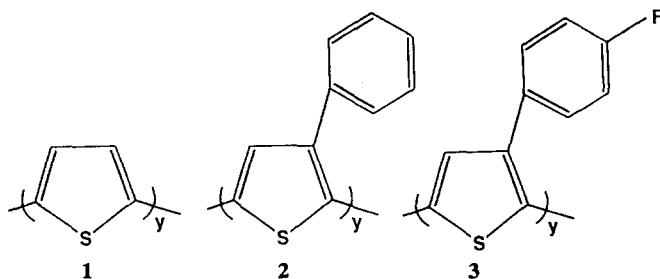


Fig. 9. Experimental results for a Type II electrochemical capacitor based on one electrode of polypyrrole/carbon paper and the other of polythiophene/carbon paper. (a) Cyclic voltammograms of the polypyrrole film (top) and the polythiophene film (bottom) at 20 mV/s (solution iR compensated). (b) Voltage-time curve recorded during 200 μ A discharge between the two polymer/carbon paper electrodes. The carbon paper electrode is 75 μ m thick and has a cross-sectional area of 0.2 cm^2 .

additional improvement in energy density for the Type II capacitor should be obtained if polyaniline were to be used in place of polythiophene, as polyaniline can be doped to a higher charge density than polythiophene over approximately the same voltage range. The disadvantage of Type II compared with Types I and III, is that it is inherently an unsymmetric system and so the poles of the device can not be reversed. This may have some negative effects on cycle life.

Type III capacitor

The advantages to a Type III capacitor, based on materials which are both n- and p-dopable, are quite clear. Nevertheless, the identification of suitable materials is far from trivial. N-doping of polyacetylene and poly-p-phenylene is quite irreversible and known in most instances to be associated with phase transformations and identifiable crystal structures of the n-doped form [21, 53]. Polythiophene (see formula 1) can be more reversibly n-doped, but only for very thin films ($< 1 \mu\text{m}$) [52].



It has been reported, however, that the n-doping of poly-3-phenylthiophene (see formula 2) is superior to that of polythiophene [23]. We have experimented with polythiophene, poly-3-phenylthiophene and a number of other poly-3-arylthiophenes in order to achieve maximum n-doping. We have observed that the n-doping of poly-3-phenylthiophene is better in terms of achievable charge density than polythiophene. However, there is still a drop off with film thickness in the specific capacity for n-doping. The best conducting polymer for high and reversible n-doping that we have discovered is poly-3-(4-fluorophenyl)-thiophene (see formula 3).

Cyclic voltammograms for polythiophene (PT), poly-3-phenylthiophene (PPT) and poly-3-(4-fluorophenyl)-thiophene (PFPT) are presented in Fig. 10 for films that p-doped comparably, to illustrate the improvements in n-dopability that we have achieved. In this case, the films were grown onto 1 cm^2 spades of 3 mil thick carbon paper at 2 mA for either 2000 seconds (PPT and PFPT) or 3000 seconds (PT), out of a solution

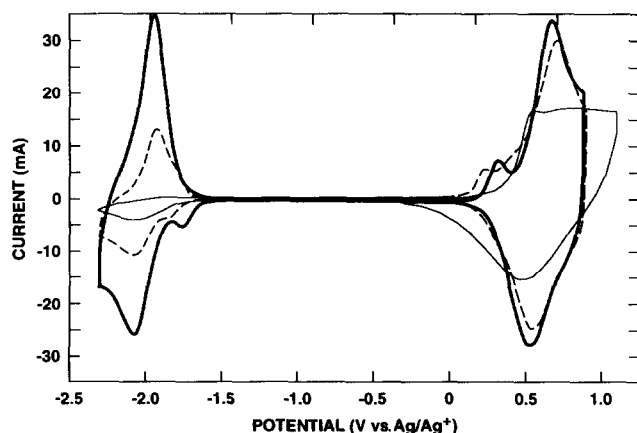


Fig. 10. Cyclic voltammograms at 25 mV/s films of (—) polythiophene, (---) poly-3-phenylthiophene, and (- - -) poly-3-(4-fluorophenyl)thiophene in 1.0 M TMAFMS in acetonitrile. The carbon paper electrode is $75 \mu\text{m}$ thick and has a cross-sectional area of 1.0 cm^2 .

of 0.1 M monomer and 1 M Et_4NBF_4 in acetonitrile. The cyclic voltammograms were then recorded for each film in 1 M Et_4NBF_4 in acetonitrile.

After optimization of the electrode-active material for the Type III scheme, we proceeded to find the most suitable electrolyte system. Acetonitrile was chosen as solvent for its wide stable voltage window and for the high solution conductivities that can be obtained as compared, for example, with propylene carbonate. Selection of the best electrolyte was more difficult. We found that n-doping of PT and derivatives is very poor in electrolyte solutions that contain alkali metal cations, and this is probably due to the large solvation shell that accompanies these ions (lithium in particular) in acetonitrile solutions. Consequently, tetraalkylammonium salts were chosen, as previous workers had successfully used them in this application [23, 52]. We found that for a film of PFPT, greater n-doping was achieved with Et_4NBF_4 than with Bu_4NPF_6 , due to the smaller size of the former cation. Hence, the natural progression was to find a tetramethylammonium salt that was soluble to high concentration (≥ 1 M), and stable over a wide voltage range. The only salt we found to satisfy these requirements was our TMATFMS ($\text{Me}_4\text{NCF}_3\text{SO}_3$). This salt does not appear to have been reported in the literature previously. The salt was obtained according to the protocol given in the Experimental section, and a 1 M solution of TMATFMS in acetonitrile has an ionic conductivity of $3.5(\pm 0.5) \times 10^{-2}$ S/cm. The improvement in n-dopability of PFPT when 1 M TMATFMS in acetonitrile is used, relative to 1 M Bu_4NPF_6 , is evident from the cyclic voltammograms presented in Fig. 11. These voltammograms were obtained for a film of PFPT grown at 2 mA for 4000 s onto a $1 \text{ cm}^2 \times 3 \text{ mil}$ ($75 \mu\text{m}$) carbon paper electrode, out of an acetonitrile solution 0.1 M in the monomer (FPT) and 1 M in TMATFMS. We have found that films of PFPT thicker than $10 \mu\text{m}$ can be p-doped and n-doped to the same high level of charge density (approximately 1 electronic charge per four monomers) in 1 M TMATFMS in acetonitrile and this performance could not be matched by either the tetrabutylammonium or the tetraethylammonium salts. We also call attention to the high degree of reversibility demonstrated here for PFPT, in both p- and n-doping, as reflected by the voltammogram recorded in the optimized electrolyte solution (Fig. 11). This degree of reversibility

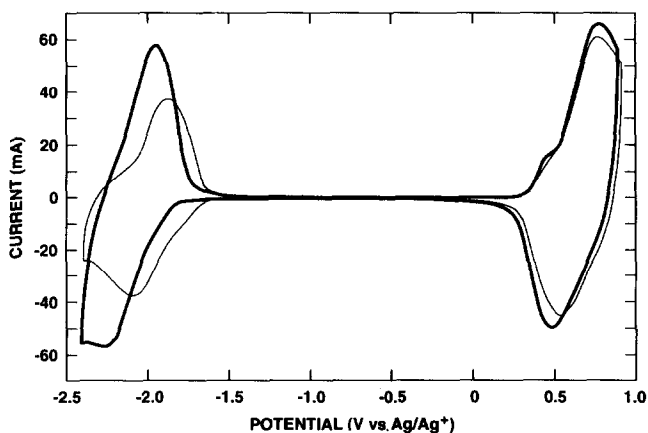


Fig. 11. Cyclic voltammograms at 25 mV/s for a film of PFPT (—) in 1.0 M TMATFMS in acetonitrile and (---) in 1.0 Bu_4NPF_6 in acetonitrile. The carbon paper electrode is $75 \mu\text{m}$ thick and has a cross-sectional area of 1.0 cm^2 .

is a significant improvement over that obtained previously for other n-dopable conducting polymers [26, 54, 55], and this explains why PFPT could be a suitable electrode material for a Type III electrochemical capacitor, whereas the other n- and p-dopable conducting polymers are not.

For the energy density test, films of PFPT were grown onto two 0.2 cm² working carbon paper electrodes out of 0.1 M FPT, 1 M TMAFMS in acetonitrile, at 1 mA for 4000 s each. The morphology of these films observed by SEM suggests that an even film of polymer grows onto the carbon fibers to some limiting thickness ($\sim 10 \mu\text{m}$), and above this the particulate type of morphology, similar to that observed with PT, starts to appear on the surface. An SEM micrograph of the broken edge of one of these electrodes is presented in Fig. 12. The cyclic voltammograms for these two films, in 1 M TMAFMS in acetonitrile, are shown in Fig. 13(a), and the capacitor cell voltage decay during a 200 μA discharge between two working electrodes is shown in Fig. 13(b). The results for the Type III capacitor can be seen in Table 1. The energy density achieved with the Type III scheme is thus about 4 times higher than that achieved with the Type I scheme.

While an energy density of 39 Wh/kg (of active material) may represent a significant breakthrough, suitability in application to electrochemical capacitors also requires demonstration of satisfactory power density. A.c. impedance spectroscopy can be used to get a measure of the resistance associated with the complete charging and discharging processes, and hence provide an indicator of potential power densities. This technique has been applied to electrochemical capacitors [15, 56] and conducting polymers [57–60] previously. Impedance spectra for PFPT, immersed in 1 M TMAFMS in acetonitrile, at two potentials which correspond to an n-doped film and a p-doped film, respectively, are presented in Fig. 14. The film was grown onto a 0.2 cm² × 3 mil (75 μm) carbon paper electrode, out of 0.1 M FPT in M TMAFMS in acetonitrile, at 1 mA for 200 s. The 23 Ω (4.6 $\Omega \text{ cm}^2$) high frequency (real) impedance intercept in Fig. 14 reflects the resistance of the bulk electrolyte between the reference electrode and the working electrode in our three-electrode cell. In a real capacitor device, there would only be a very thin layer of this electrolyte between the two electrodes, and at a separator thickness of 4 mil (0.1 mm), the electrolyte is expected to contribute about 1 $\Omega \text{ cm}^2$ to the overall series resistance of the cell. The most important features of

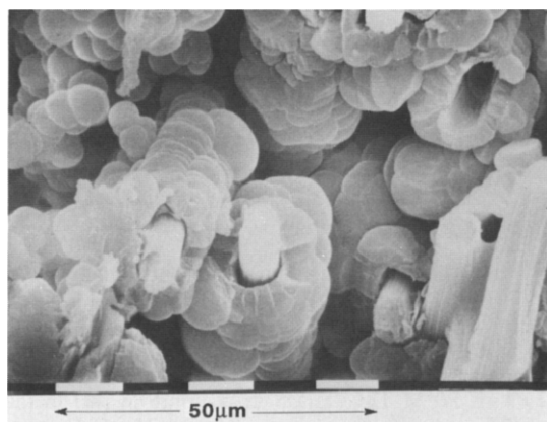


Fig. 12. Scanning electron micrograph at a broken edge of one of the PFPT/carbon paper electrodes used in the Type III capacitor experiment.

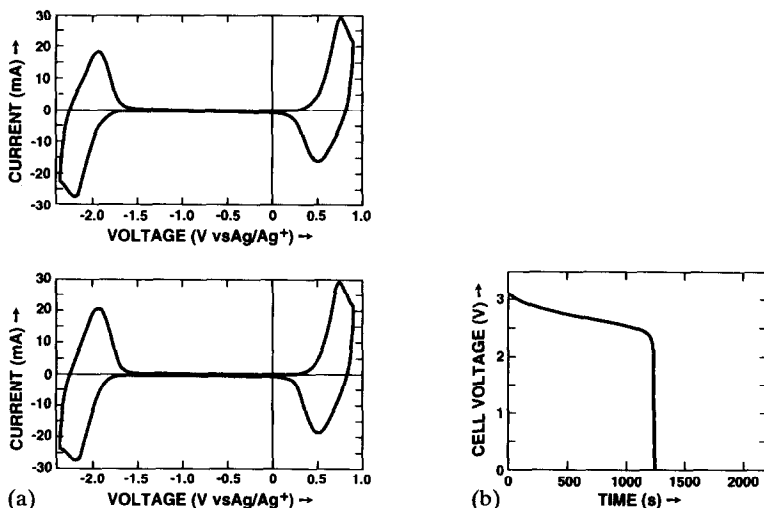


Fig. 13. Experimental results of for a Type III electrochemical capacitor constructed with two identically grown films of PFPT in a solution of 1.0 M TMAFMS in acetonitrile. (a) Cyclic voltammograms of the two PFPT films at 20 mV/s (solution iR compensated). (b) Voltage–time curve recorded during 200 μ A discharge between the two polymer/carbon paper electrodes. The carbon paper electrode is 75 μ m thick and has a cross-sectional area of 0.2 cm^2 .

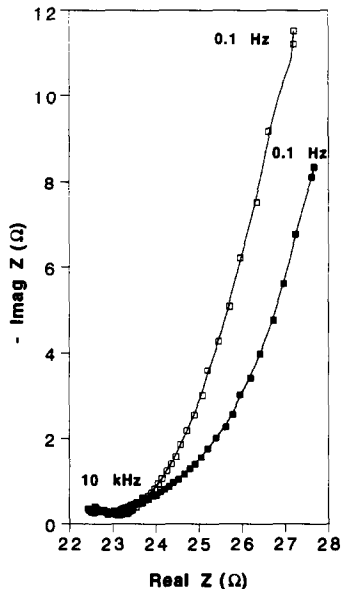


Fig. 14. Impedance spectra of a film of PFPT in 1.0 M TMAFMS in acetonitrile (■) in the n-doped state at -2.1 V vs. Ag/Ag^+ , and (□) in the p-doped state at $+0.8$ V vs. Ag/Ag^+ . The polymer film was electrodeposited onto a 0.2 cm^2 , 75 μ m thick carbon paper electrode out of 0.1 M FPT in 1.0 M TMAFMS in acetonitrile, at 1 mA for 2000 s.

the impedance spectra in Fig. 14 are the low resistances associated with the transport process within the porous structure of the electrode. These resistances are evaluated from the difference in the real part of the impedance between low and high frequency [15], and are seen from Fig. 14 to be only about $0.8 \Omega \text{ cm}^2$ for the p-doped film of PFPT and about $1.0 \Omega \text{ cm}^2$ for the n-doped film. These values are very low, particularly considering the non-aqueous electrolyte employed here, and demonstrate the good quality of the electrodes fabricated by electrodeposition of the active-conducting polymer on the carbon paper substrate. Based on these impedance spectra, we can conservatively estimate the overall internal resistance of a capacitor cell based on PFPT to be about $3 \Omega \text{ cm}^2$. (We would not expect electronically conducting components of the device, i.e., carbon paper, bipolar plates, and current collectors, to contribute significantly to the internal resistance of the cell – the ohmic resistance through the 3 mil carbon paper, for example, is only approximately $5 \times 10^{-5} \Omega \text{ cm}^2$.) The approximate capacitance for a device constructed from two electrodes such as this was measured at 1.2 F/cm^2 . Hence, we estimate an RC time constant associated with discharge of a capacitor cell to be about 4 s. From this we obtain an effective power density (energy density \div time constant) of 35 kW per kg of active material on both electrodes. This is more than an order of magnitude higher than the goal power density for the total device in transportation applications [16]. Clearly, because of the dependence of charge/discharge dynamics on active-material loading, this high power density is significant only if achieved in conjunction with a significant energy density. In our case, the effective power density of 35 kW/kg projected according to the impedance measurements in Fig. 14, was recorded for an active-conducting polymer film with capacitive energy storage of 1.75 J per cm^2 of electrode area. For a cell thickness of 11 mil ($275 \mu\text{m}$), readily achievable with these 3 mil ($75 \mu\text{m}$) thick electrodes, this corresponds to 65 J per cm^3 of the device, which is very close to the current goal of the US Department of Energy (DOE) for volumetric energy density in an electrochemical capacitor for EV applications [16]. While impedance analysis can provide a good estimate of accessible power densities, practical values need to be obtained from complete charge/discharge cycles and we are currently working to this aim.

Conclusions

Conducting polymers represent an attractive class of materials for use as active components in electrochemical capacitors. Deposition of the polymer on a porous carbon paper support can be performed electrochemically yielding layers of high charge density and low charging impedance. While micrographs shown in this paper demonstrate high porosity on the micron scale, other investigations [61] have demonstrated that these conducting polymer films have high porosity also on the nanometer scale, which explains the ability to charge at high rates up to levels of one electronic charge per 2–4 molecular units. The voltage of the device can be extended higher than 3 V by employing n- and p-dopable polymers in non-aqueous electrolytes. Optimization of this type of conducting polymer, and of the electrolyte, has resulted in significant improvement in the extent and reversibility of charging in both p- and n-doping modes. We believe these are the best results presented for dual reversible doping of a conducting polymer film. With this system, high energy densities in capacitive electrochemical processes can be achieved. Results from impedance spectroscopy, aimed at providing information on the accessible power densities, suggest that this technology will be well suited for high power applications. We have described how our systems compare

favorably, in terms of energy and cost, with currently available technologies. We have demonstrated 39 Wh/kg and have estimated 35 kW/kg of active material, respectively, to be compared with U.S. DOE goals of 5 Wh/kg and 0.5 kW/kg of total device, respectively. If satisfactory cycle life can be demonstrated for these materials in real devices, they may represent the best suited class of materials for electrochemical capacitors currently available. We are now expanding our experiments to include the testing of more realistic capacitor devices, for total energy density, power density and cycle life.

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Appendix

On the distinction between 'electrochemical capacitors' and 'batteries'

One can argue that the electrochemical devices described here as Type I, II and III electrochemical capacitors can be equally well, or even better described as batteries. (Such arguments were made by the reviewers of this paper.) In particular, the sharp drop in cell voltage at the end of discharge in the case of the Type III capacitor (Fig. 13), resembles more a battery discharge curve than a typical (linear) capacitor discharge curve. There are, however, other diagnostic criteria which make the Type III device, much as Types I and II, a legitimate member of the electrochemical capacitor family. Before advancing further with the explanation for our preferred terminology, we agree that this is to large extent a matter of semantics. One may choose to draw the demarcation line between electrochemical capacitors and batteries differently.

The criteria which we suggest for distinction between electrochemical capacitors and batteries are: (i) the fundamental nature of the charge/discharge process; (ii) the typical combination of energy and power density levels required, and (iii) the nature of the interfacial impedance. In terms of the fundamental process of charge/discharge, we suggest that the demarcation line between electrochemical capacitors and batteries is that in the former only translation of electronic and ionic charges within the solid and electrolytic domains, respectively, takes place during charge/discharge in the composite active layer. In contrast, a battery charge/discharge process involves also significant phase generation/elimination or phase transformation. A possible counter argument could be that 'redox processes' take place in the conducting polymer as it charges and discharges, therefore it is a battery. However, because of the high mobility of the electronic charges in the doped form of polymers like polypyrrole, polyaniline or polythiophene, the excess electronic charge ends up in a highly delocalized state. Therefore, charging of the polymer backbone is not very different than charging of the metal (or carbon) side of a metal/electrolyte interface. In fact, descriptions of the doping process have been given in terms of a free electron (one dimensional electron band) model, which is supported by ESR measurements of spin density and spin mobility in the conducting polymer [62].

Our second criterion has to do with the niche that electrochemical capacitors are expected to fill in terms of the combined energy and power density levels of the device [15, 16]. The special requirement from an electrochemical capacitor is to provide a power density significantly higher than that of a battery (in the kW/kg range) for a relatively short period of time of the order of 10–20 s. This defines the required energy density around 5–10 Wh/kg, i.e., significantly smaller than that of advanced batteries but significantly larger than that of conventional capacitors. Based on measured energy densities and interfacial impedances, all three types of systems discussed in this paper are projected to fall within this energy/power density niche. Again, one may claim that what is described here is a battery with a discharge rate of 200 to 300 C, but this high discharge rate is not so typical for batteries.

The last criterion suggested by us is based on the electrical behavior of the interface. The Type III electrochemical capacitor, as much as Types I and II, fulfills the requirement that, at a frequency around 0.1 Hz, the phase angle of the interfacial impedance approaches 90°, i.e., approaches capacitive behavior. The choice of this particular frequency obviously has to do with the requirement of completion of charge, or discharge, within 10 s. The phase angle of the interfacial impedance in an electrochemical capacitor will be lower at frequencies significantly higher than 0.1 Hz [15], a feature which distinguishes this device from a conventional capacitor.

Finally, let us add that suggestions for new unique terminology ('Capattery'*, 'ultracapacitor' or 'pseudocapacitor') have been made for devices of this general type. However, the preferred terminology at the last '*International Seminar on Double Layer Capacitors and Similar Energy Storage Devices*', Florida, 1992, seemed to be 'electrochemical capacitor'.

*'Capattery' is a trademark of Evens, Inc., used for double-layer capacitors based on activated carbon.