

## Polymer-based supercapacitors

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### Abstract

The use of electronically conducting polymers (ECPs) as pseudocapacitive electrode materials in high-power supercapacitors is a challenge to overcome the performance of carbon-based double-layer supercapacitors for applications requiring high power levels. ECPs provide different supercapacitor configurations but devices with the polymer n-doped form as the negative electrode and the p-doped form as the positive one are the most promising in term of energy and power. This type of supercapacitor has indeed a high operating voltage, it is able to deliver all the doping charge and it has in the charged state both electrodes in the conducting (p- and n-doped) states. Data for poly(3-methylthiophene) positive and negative electrodes, envisioned for a n/p-type supercapacitor, as well as data for cyclability of supercapacitors with composite electrodes based on such conventional polymer are here reported and discussed. The capacitance and cycling stability of poly(3-methylthiophene) are sufficiently high to take this polymer into consideration for supercapacitor technology. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Conjugated polymers; Electronically conducting polymers; Polymer-based supercapacitors; Poly(3-methylthiophene); Supercapacitors

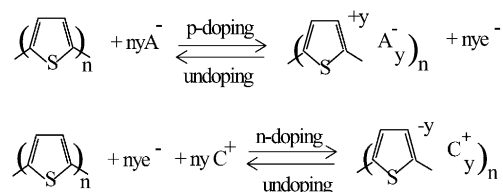
### 1. Introduction

Supercapacitors characterized by high capacitance values in the Farad ranges and low internal resistance are devices for applications requiring high-current loads. The enormous progress in supercapacitor technology, resulting in electrode materials with higher and higher specific capacitance values, has led to an extension of their application range to the battery market. Supercapacitors can be used as un-interruptable power sources (UPS), can be coupled with batteries to provide peak power, can replace batteries for memory back-up; Table 1 shows some of their feasible applications in the low (<10 V) and high (>10 V) voltage ranges. Many applications are for the electronics consumer market, which requires devices delivering up to 1 F. The world-wide market for supercapacitors in 1999 was of about US\$ 115 million (78% covered by the low-voltage devices), and this value is forecast to double by the year 2004. By comparison, the 1999 global market for capacitors was about US\$ 11 and 22 billion for batteries.

The high-performance supercapacitors on the market are double-layer carbon supercapacitors (DLCs) based on activated carbon of high specific area (1500–2400 m<sup>2</sup> g<sup>-1</sup>); some of the main producers are Matsushita,

Tokin, Elna, and NEC. Advances in DLCs are expected by lowering their equivalent series resistance (ESR) and cost, with research activity mainly focusing on the development of new activated carbon as well as on new device designs.

Research is also investigating other classes of electrode materials, the challenge being to come up with devices that outperform the DLCs; one promising class is that of electronically conducting polymers (ECPs). Energy storage in ECP supercapacitors is not electrostatic in origin as in DLCs, but is due to a Faradaic process which takes place at the electrode materials, as in a battery, giving rise to what is called pseudocapacitance. After the charge-transfer process, called the doping process, the polymers become electronically conductive. The following scheme shows the p- and n-doping–undoping processes, i.e. the processes in which a polymer (the polythiophene is an example) is reversibly oxidized and reversibly reduced.



Given that the doping–undoping, i.e. the charging–discharging process of ECPs, is associated with the insertion–deinsertion of counter-ions (A<sup>-</sup> and C<sup>+</sup>) coming from the

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Table 1  
Applications for supercapacitors in the low and high voltage range

Low voltage (<10 V)	High voltage (>10 V)
Memory protection in CMOS logic circuits, VCRs, CD players, video cameras, clock radios, PCs UPS in security alarm systems, remote sensing, smoke detectors	UPS, engine starting, audio base-line stiffeners, electric vehicles Mechanical actuators, solar energy array equipment, transportation infrastructure equipment, military/aerospace market

electrolyte, ECPs may also be depicted as ion-insertion materials.

The distinction between an ECP supercapacitor and a battery is not very sharp. A criterion that can be used to distinguish them might be the role they are called on to play in terms of specific energy and power. A supercapacitor is expected to deliver a high specific power for a short period of time (10–100 s), and an energy significantly lower than that of the batteries.

ECPs are promising electrode materials for supercapacitors for two main reasons: (i) they are materials of high specific capacitance, because the charge process involves the entire polymer mass; (ii) they are materials of high conductivity in the charged state, so that devices with low ESR are feasible. In addition, their plastic properties readily enable their manufacture as thin film, and their cost is lower than that of activated carbons when conventional ECPs are considered.

The main question arising over the use of ECPs as electrode materials in supercapacitors concerns their cycling stability, which has to be as long as that required by the envisioned applications of these devices. Polymer cycling stability could limit their use with respect to that of the activated-carbon supercapacitors which are not affected by this problem, since they are based on an electrostatic process of charge–discharge. The ECP charge–discharge process, which involves insertion–deinsertion of ions in a way resembling that of the lithium-ion batteries, could limit the cycle life of ECP supercapacitors. However, due to the plastic nature of ECPs, the mechanical stress of such materials that results from the volume changes during the ion insertion–deinsertion process should not significantly affect the device life.

The present study reports and discusses key data for poly(3-methylthiophene) (pMeT) positive and negative electrodes envisioned for a n/p-type supercapacitor as well as for cyclability of n/p supercapacitors with composite electrodes based on such conventional polymer.

## 2. Experimental

Two kinds of pMeT-based electrodes were prepared: pMeT/Pt electrochemically synthesized at room temperature in  $\text{CH}_3\text{CN}$ –0.5 M  $\text{Et}_4\text{NBF}_4$ –0.1 M MeT at  $10 \text{ mA cm}^{-2}$ , and composite electrodes prepared by dry-mixing pMeT, carbon (conducting additive) and Cmc (binder) and pressed on stainless steel current collectors, as described in [1,2]. The pMeT/Pt electrodes were tested by cyclic voltammetry

(CV) in propylene carbonate (PC)–0.2 M  $\text{Et}_4\text{NBF}_4$  and by galvanostatic charge–discharge cycles in ethylene carbonate/dimethylcarbonate (EC/DMC) (1:1)–0.2 M  $\text{LiBF}_4$ . The composite electrodes were used to assemble supercapacitors with PC–0.2 M  $\text{Et}_4\text{NBF}_4$ , as in [1,2]. The cyclability performance of the supercapacitors was tested by repeated charge–discharge galvanostatic cycles in selected potential ranges. The electrochemical experiments on pMeT/Pt electrodes and supercapacitors were performed at room temperature in a MBraun Labmaster 150 dry box ( $\text{H}_2\text{O}$ ,  $\text{O}_2 < 1 \text{ ppm}$ ) with a PAR 273A potentiostat/galvanostat and a 545 AMEL galvanostat/electrometer. All the potential values were measured versus Ag (a quasi-reference electrode) and expressed versus saturated calomel electrode (SCE).

## 3. Results and discussion

While ECPs provide different supercapacitor configurations, devices with the n-doped polymer as the negative electrode and the p-doped as the positive one (n/p-type) are the most promising in terms of energy and power, and the only ones able to outperform the DLCSs. Indeed, the n/p-type supercapacitor has a high operating voltage (ca. 3 V), can deliver all the doping charge, and in the charged state has both electrodes in the conducting (p- and n-doped) states. High working potentials such as 3 V, which are related to the energy gap between the valence and conduction bands of the polymers, are attainable only in organic electrolytes. Electrolyte optimization, even in terms of salt concentration, is an important target since in n/p-type supercapacitors, as in DLCSs, salt consumption occurs during device charge. An optimized cell design requires a salt concentration sufficiently high so as not to limit the electrode's capacitance and so as to assure a high conductivity after the device charge to minimize the ionic component of its ESR. The salt must be an alkylammonium, because the n-doping of ECPs is unattainable with lithium salts. Thus, PC– $\text{Et}_4\text{NBF}_4$ , which is also widely used in DLCSs, is a viable candidate as electrolytic medium: it can work from  $-20$  to  $80^\circ\text{C}$  and is environmentally friendly.

ECPs undergoing p- and n-doping inside the electrochemical stability window of the electrolyte enable the realization of symmetric n/p-type supercapacitors: the thiophene-based family meets this requirement and has the advantage of a high environmental stability in the undoped form. By adding suitable substituents to tune the potentials at which the p- and n-doping processes occur, the engineering

of the thiophene unit leads to heavier molecules and higher cost. Polymers based on heavy thiophene-derivative require higher doping levels than polythiophene to meet the criterion of high specific capacitance, and this can adversely affect the polymer cycle life because of the greater mechanical stress.

It may thus be useful to turn our attention back to a conventional thiophene-based polymer such as pMeT. There is an extensive literature on its preparation: in suitable polymerization conditions, it is possible to prepare a polymer material with high conjugation length and high conductivity of the p-doped form.

The electrochemical characterization of the polymer materials should be performed with electrodes of the same thickness as that envisioned for the final device, and we estimated a practical ECP mass in the range from 3 to 12 mg cm<sup>-2</sup>. We carried out a study in PC–0.2 M Et<sub>4</sub>NBF<sub>4</sub> of pMeT/Pt electrodes of weight in this range by CVs at 20 mV s<sup>-1</sup> in the p- and n-doping potential domains (from –0.50 to 1.40 V versus SCE and from –0.55 to –2.55 V versus SCE, respectively). To gain greater insight into the specific capacitance values of this polymer and to get a rough estimate of the specific energy of a symmetric n/p-type supercapacitor based on it, diagrams (from the CVs) were constructed in which the electrode potential was plotted against the p- and n-doping charges ( $Q_d$ ) calculated from the CVs by integration of the current density (during discharge) as in [3]. Table 2 reports the capacitance (in F g<sup>-1</sup>) and the capacity (in mAh g<sup>-1</sup>) for p- and n-doped pMeT electrodes with a polymer mass of 3.3 mg cm<sup>-2</sup>, and the specific energy value for the device. The capacitance values of both the p- and n-doped forms of pMeT are significantly high, with the polymer performing better as positive electrode. Hence, in a symmetric n/p pMeT supercapacitor, the negative electrode limits device capacitance, and for a supercapacitor having both electrodes of the same mass (3.3 mg cm<sup>-2</sup>), a viable specific energy is 25 Wh kg<sup>-1</sup>. Moreover, in the tested potential range, the p-doped pMeT's high capacity values approached the theoretical one that, for thiophene-based polymers with doping level in the range 0.3–0.35, is estimated at about 100 mAh g<sup>-1</sup>.

To answer the question of the polymer's cycling stability, we tested by repeated CVs (up to 1000 cycles) the p-doping–undoping of pMeT, which occurring in a safer potential range than that of the n-doping with respect to the electrolyte electrochemical stability window, requires less drastic control of the operating conditions. Fig. 1 shows that the pMeT

Table 2

Capacity ( $Q_d$ ), capacitance ( $C$ ) of pMeT/Pt electrode ( $Q_{el} = 7.5 \text{ C cm}^{-2}$ , 3.3 mg cm<sup>-2</sup>) and specific energy of the symmetric device ( $E$ ) from CV at 20 mV s<sup>-1</sup> in PC–0.2 M Et<sub>4</sub>NBF<sub>4</sub>

pMeT/Pt	$Q_d$ (mAh g <sup>-1</sup> )	$C$ (F g <sup>-1</sup> )	$E$ (Wh kg <sup>-1</sup> )
p-doped	70	240	25
n-doped	30	180	

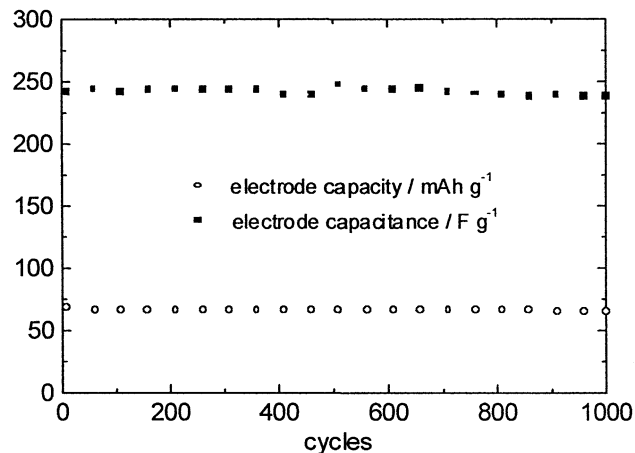


Fig. 1. Capacity (○, mAh g<sup>-1</sup>) and capacitance (■, F g<sup>-1</sup>) of a pMeT/Pt electrode ( $Q_{el} = 7.5 \text{ C cm}^{-2}$ , 3.3 mg cm<sup>-2</sup>) from CV at 20 mV s<sup>-1</sup> in PC–0.2 M Et<sub>4</sub>NBF<sub>4</sub>.

as positive electrode is able to sustain 1000 cycles without any fade in capacity (mAh g<sup>-1</sup>) and capacitance (F g<sup>-1</sup>). Even if the number of cycles in Fig. 1 is far from the cycle life usually required for supercapacitors, these results provide a first positive answer to the question of ECP cycling stability.

To investigate the cyclability performance of the pMeT positive electrode under different galvanostatic conditions, we carried out preliminary tests in a Li/pMeT cell with a lithium metal negative electrode of large area to avoid kinetic limitations due to the counter-electrode itself. Fig. 2 shows discharge curves of the cell with EC/DMC (1:1)–0.2 M LiBF<sub>4</sub>, charged and discharged at 8, 16, and 24 mA cm<sup>-2</sup> (with respect to the pMeT electrode area) with 2.4–4.7 V cut-off potentials. In spite of the high ohmic drop in galvanostatic profiles, which is related to the 4 mm electrode distance, the results demonstrate that the p-doped pMeT electrode maintains its high capacitance value even at high current density.

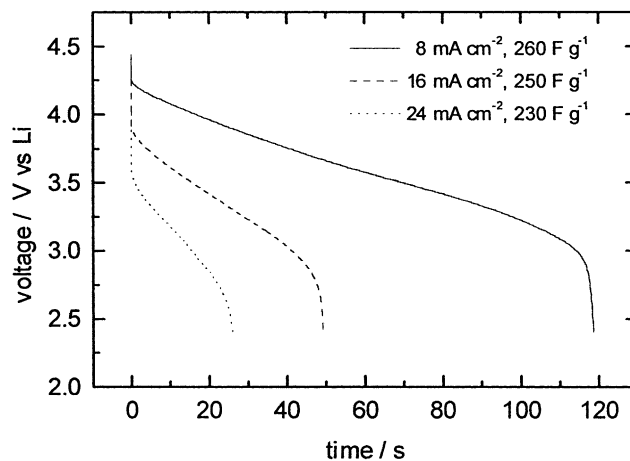


Fig. 2. Discharge curves of a Li/EC/DMC (1:1)–0.2 M LiBF<sub>4</sub>/pMeT/Pt ( $Q_{el} = 7.5 \text{ C cm}^{-2}$ , 3.3 mg cm<sup>-2</sup>) cell at 8, 16, and 24 mA cm<sup>-2</sup> (pMeT area), cut-off potentials 2.4–4.7 V.

Table 3  
Electrode composition of the different (–)pMeT/pMeT(+) supercapacitors based on composite electrodes

Code	Negative electrode				Positive electrode			
	ECP		C (%)	Cmc (%)	ECP		C (%)	Cmc (%)
	%	mg cm <sup>-2</sup>			%	mg cm <sup>-2</sup>		
S1	30	8.3	55	15	30	3.3	55	15
S2	30	9.2	55	15	55	6.8	30	15

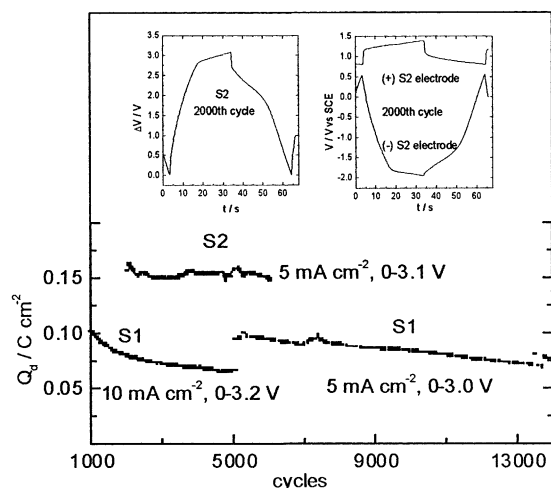


Fig. 3. Delivered charge of supercapacitor S1 [(–)pMeT 30%/pMeT 30%(+)] and S2 [(–)pMeT 30%/pMeT 55%(+)] vs. cycle number from galvanostatic charge–discharge cycles in  $\text{PC}-0.2 \text{ M Et}_4\text{NBF}_4$  with different current densities and cut-off potentials. The inset shows the voltage profile of a charge–discharge cycle of supercapacitor S2 and of each electrode during the 2000th galvanostatic charge–discharge cycle at  $5 \text{ mA cm}^{-2}$  in  $\text{PC}-0.2 \text{ M Et}_4\text{NBF}_4$ , cut-off potentials 0.0 and 3.1 V.

We then assembled and tested by galvanostatic charge–discharge cycles at different current densities, symmetric n/p-type devices with composite electrodes: these were based on pMeT, carbon-conducting additive and binder, and pressed on stainless steel grids as current collectors. These supercapacitors with  $\text{PC}-0.2 \text{ M Et}_4\text{NBF}_4$  sustained several thousands of cycles with a coulombic efficiency approaching 100%. Fig. 3 shows the delivered charge versus cycle number for two supercapacitors with different electrode compositions and electrode masses (reported in Table 3). As an example, Fig. 3 also displays the charge–discharge curve of the 2000th galvanostatic cycle of the S2 supercapacitor at  $5 \text{ mA cm}^{-2}$  and the corresponding voltage profiles of each electrode checked against a reference electrode. These profiles indicate that both electrodes work in safe potential ranges with respect to the electrolyte stability window and show a high ohmic drop that, being related to a non-optimized cell design in terms of electrode distance (1 mm), can be significantly lowered.

We also carried out CVs on pMeT composite electrodes in which the percentage of the conducting additive was reduced to increase that of ECP. These measurements demonstrate

that the carbon content can be significantly lowered to 10% for the positive pMeT electrode and to 30% for the negative pMeT one without affecting electrode cyclability performance. These data confirm the higher conductivity of the p-doped pMeT with respect to the n-doped one, and may explain its higher performance as positive electrode.

#### 4. Conclusions

Our results, while referring to devices of non-optimized design especially in terms of electrolyte thickness, salt concentration, and percentage of ECP content in the composite electrodes, clearly demonstrate that thousands of cycles, with delivered charge of hundreds of  $\text{mC cm}^{-2}$ , are attainable with ECP supercapacitors. The capacitance and cycling stability of pMeT are sufficiently high to take conventional thiophene-based polymers into consideration for supercapacitor technology, at least for the positive electrode. A hybrid configuration with pMeT as positive and activated carbon as negative electrode may even yield a promising device both in terms of performance and cost.

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