

Polythiophene-based supercapacitors

Alexis Laforgue, Patrice Simon ^{*}, Christian Sarrazin, Jean-François Fauvarque

Laboratoire d'Electrochimie Industrielle du CNAM, 2 rue Conté, 75003 Paris, France

Abstract

Polythiophene (Pth) and polyparafluorophenylthiophene (PFPT) have been chemically synthesized for use as active materials in supercapacitor electrodes. Electrochemical characterization has been performed by cyclic voltammetry and an electrode study has been achieved to get the maximum capacity out of the polymers and give good cyclability. Specific capacity values of 7 mAh g^{-1} and 40 mAh g^{-1} were obtained for PFPT and polythiophene, respectively. Supercapacitors have been built to characterize this type of system. Energy storage levels of 260 F g^{-1} were obtained with Pth and 110 F g^{-1} with PFPT. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Supercapacitors; Polythiophene

1. Introduction

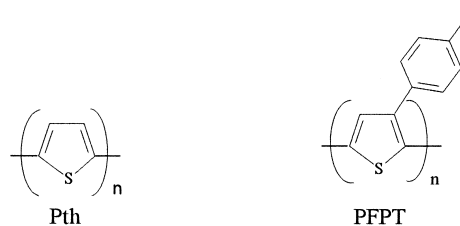
In the research fields of energy storage, and more specifically of supplying high powers, electrochemical supercapacitors have been among the most studied systems for many years [1–4].

One of the possible applications is in electric vehicles. We have been working on electronically conducting polymers for use as active materials for electrodes in supercapacitors. These polymers have the ability of doping and undoping with rather fast kinetics and have an excellent capacity for energy storage (350 F g^{-1} for polypyrrole, 250 F g^{-1} for polythiophene).

The aim of this work was to fabricate a high energy density (10 Wh g^{-1}) 3 V supercapacitor using electronically conducting polymers (ECP). Polythiophene (Pth) appeared to be capable of such a voltage value, as it could be negatively or positively doped. Previous work had shown that negative doping of Pth appeared at very negative potential values, where electrolyte reduction occurred. So, it was decided to use one of its derivatives, polyparafluorophenylthiophene (PFPT), as the negative electrode. (–ve) PFPT//electrolyte//Pth (+ve) systems were then studied, where PFPT cycled within its negative doping (n-doping) potential range, and Pth in its positive doping (p-doping) domain.

The most important part of the studies on ECP described in the literature have been focused on electro-syn-

thesized polymers, made by electro-oxidation of the monomer when dissolved in an electrolyte [5–7]. These are synthesized directly onto the current collector, but the thickness of these electrodes cannot exceed $100 \mu\text{m}$. This way, the fabrication of large electrodes is not easy to achieve. It was therefore decided to chemically synthesize the polymers, in order to obtain powders that were easier to manipulate during the making of the electrodes.



2. Experimental

2.1. Polymer synthesis

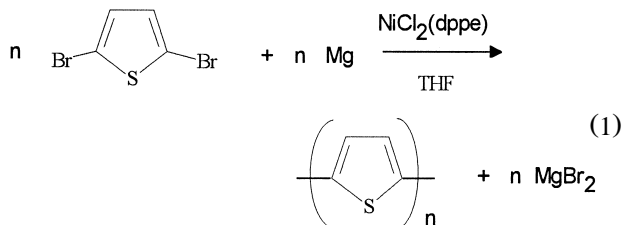
Polythiophene (Pth) was synthesized by polycondensation of 2,5-dibromothiophene in THF, in the presence of magnesium, and catalyzed by NiCl_2 (diphenylphosphino ethane) [8].

Magnesium was introduced into a round bottom flask containing the THF, and the solution was stirred under an argon atmosphere. The dibromothiophene was added slowly (without air contact) and a Mg-insertion reaction occurred at each halogen bond (Eq. (1)). Polymerization

^{*} Corresponding author. Fax: +33-1-40-27-26-78; tel.: +33-1-40-27-24-20; E-mail: simon@cnam.fr

was performed by carefully adding the catalyst to the solution. The reaction began immediately and was completed in one hour. After filtering to obtain the polymer, which appeared as a red powder, it was washed several times with methanol to get rid of the oligomers and the catalyst.

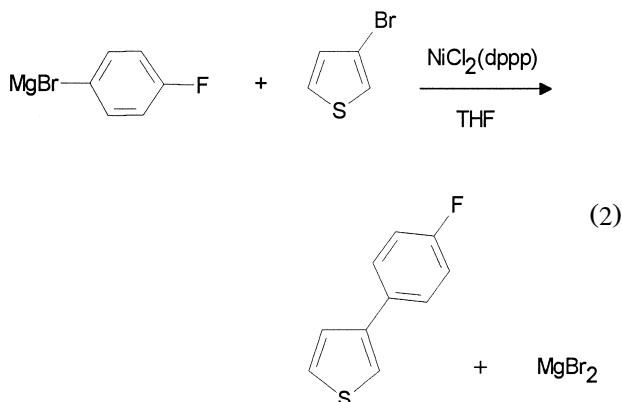
The reaction yield was approximately 90% in weight.



Parafluorophenylthiophene (FPT), the monomer of PFPT, was synthesized by a coupling reaction of 3-bromothiophene and 4-fluorophenylmagnesium bromide in THF with NiCl_2 (diphénylphosphino propane) as catalyst [9,10] (Eq. (2)).

The bromothiophene was placed in a round bottom flask with the catalyst, in a glove box filled with argon. The solution was stirred and kept at -10°C . Fluorophenyl magnesium bromide (1 M in THF) was added to the solution with a syringe (no air contact). The mixture was stirred for 12 h and then the reaction stopped by adding carefully 1 M HCl to neutralize the excess of fluorophenyl magnesium. The organic phase was filtered to obtain the monomer which appeared as a yellow powder. Recrystallization was performed by dissolving the monomer in methanol and precipitating it with water. FPT was a white powder.

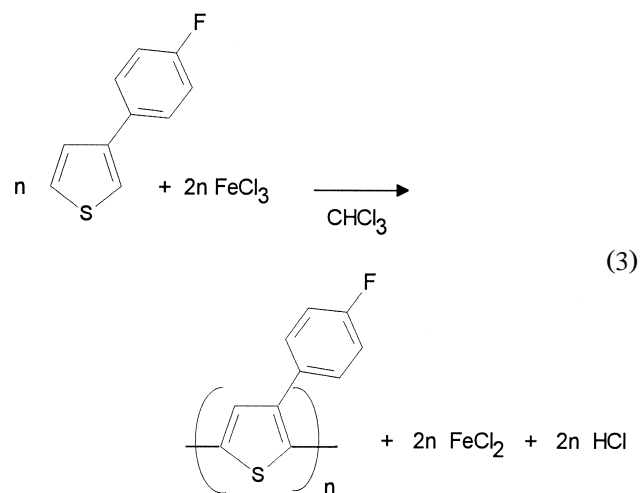
The yield from this reaction was always more than 90 wt.%.



FPT was polymerized by a direct oxidation with FeCl_3 as oxidant in chloroform (Eq. 3). This method had been

already used to polymerize pyrrole, thiophene and arylthiophenes [11–14]. A suspension of anhydrous iron (III) chloride in chloroform was prepared in the round bottom flask. The suspension was placed under argon and stirred at ambient temperature (23°C). The solution potential was then $+1.25 \text{ V/ECS}$ (the monomer oxidation occurs at $+0.9 \text{ V/ECS}$). FPT was dissolved in chloroform and added in the medium with a molar ratio of $n_{\text{FeCl}_3}/n_{\text{FPT}} = 4$. Polymerization was performed for 2 h before stopping it by addition of methanol, which neutralizes the FeCl_3 still present in the solution (probably by dimerization of the FeCl_3 which had then no more oxidative power) [15]. The polymer was then filtered and washed several times with methanol to remove the residual chloride ions from the PFPT.

The yields obtained for these reactions were near 80 wt.%.



2.2. Characterization

As these polymers are quite insoluble in any known solvent, their chemical characterization was difficult. It was decided to test them in a way representative of their future use as active materials for energy storage devices: cyclic voltammetry was used to compare their electrochemical properties.

Cyclic voltammetry on the polymers was performed in acetonitrile using different salts (NEt_4^+ , CF_3SO_3^- , NEt_4^+ , CH_3SO_3^-), in the n- and p-doping domain, for PFPT and Pth. The reference electrode used was Ag^+/Ag , made of a silver wire in a solution of 10^{-2} M AgNO_3 in acetonitrile. Its potential of this electrode is $+0.2 \text{ V/ECS}$. The counter electrode was a 4 cm^2 platinum foil for primary characterization and an over-capacity polymer electrode bound onto metallic grids for the cyclability tests. This over-capacity electrode was used to settle the counter electrode potential and thus prevent electrolyte degradation reactions on this electrode.

The potentiostat used was an EG & G PAR Model 273A, coupled to a computer. Galvanostatic cycling was achieved with a Biologic MacPile and resistance measurements were made using a HP 4338B milliohmmeter or an impedance meter (Solartron Schlumberger 1255) at 1000 Hz.

Two types of working electrodes were used. The first one (referred as 'enclosed electrodes') was made of a mixture of polymer and graphite powders, enclosed and pressed into a metallic grid. This technology allowed the qualitative characterization of the polymers. Graphite was used to maintain a good conductivity inside the electrode in the range of potentials where the polymers show insulating properties. In the second type of electrode, the active materials (polymer and conductor) were mixed with different binders [carboxymethylcellulose (CMC), polyvinylidene fluoride (PVDF), polytetrafluoroethylene, (PTFE)] and pasted onto metallic current collector grids, to quantitatively characterize the polymers. All the tests were carried out in an argon atmosphere.

3. Results and discussion

3.1. Doping processes

Fig. 1 presents the cyclic voltammetry of a Pth and a PFPT electrode.

The negative doping appears as a reduction wave at low potentials: -1.8 V/ref for PFPT and -2.2 V/ref for Pth. It corresponds to the injection of electrons into the polymer and to the insertion of cations from the electrolyte into the electrode to preserve the electroneutrality (Eq. (4)). This leads to a change in the electronic structure of the polymer and it becomes electronically conductive. The negative undoping process appears as an oxidation peak on

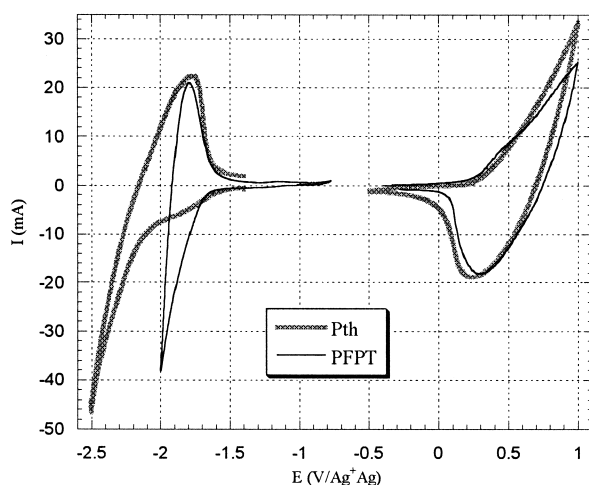
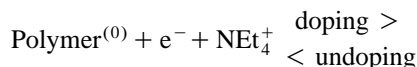


Fig. 1. Cyclic voltammograms of the doping processes of Pth and PFPT. Sweep rate: 20 mV s^{-1} , electrolyte 1 M NEt_4^+ , CF_3SO_3^- in acetonitrile. The curves are rescaled to be comparable.

the reverse scan, at -1.8 V/ref for both polymers and corresponds to electron extraction from the polymer, and to the removal of cations. The polymer returns to its neutral and isolating state.



It is important to note that the n-doping process of the Pth occurs at more negative potentials than it does for PFPT. As the electrolyte reduction begins at -2.3 V/ref on a platinum electrode, it was decided to use the PFPT as the negative active material to minimize degradation of the electrolyte. The fluorophenyl group (electron acceptor substituent) confers to PFPT a higher and more stable n-doping process leading to a better cyclability than Pth.

For the positive doping, the same process of insertion of ions occurs, but the electrons are now extracted from the polymer and anions are inserted in the electrode (Eq. (5)). The p-doping of both polymers appears as an oxidation wave beginning at 0.3 V/ref and the undoping as a reduction peak at 0.3 V/ref for PFPT and 0.2 V/ref for Pth. It represents the removal of anions while electrons are injected into the polymer.



Both polymers can be used as positive active material for supercapacitors, since they have almost the same p-doping domains, but Pth is more capacitive than PFPT (250 F g^{-1} and 110 F g^{-1} , respectively). It was therefore decided to choose Pth as the positive active material.

From the cyclic voltammograms of Fig. 1, it can be seen that a supercapacitor made up of a Pth positive electrode and a PFPT negative electrode should present a nominal voltage of 3 V in the charged state, which corresponds to a potential of -2 V/ref for the PFPT and $+1$ V/ref for the Pth. This system should be able to deliver all its capacity between 3 V and 1.5 V, the latter voltage corresponding to the difference of potential between the end of the n-undoping process of the PFPT (-1.5 V/ref) and the end of the p-undoping process of the Pth (0 V/ref).

3.2. Polymer characterization

Fig. 2 presents the cyclic voltammogram of PFPT between -1 V/ref and -2 V/ref. The electrode was made up of 50% of polymer and 50% of graphite, enclosed in an aluminium grid. -2 V/ref was determined as the minimum potential to ensure a good cyclability to the polymer. Above this potential, the cyclability is guaranteed by the absence of reduction of the electrolyte. More than 500

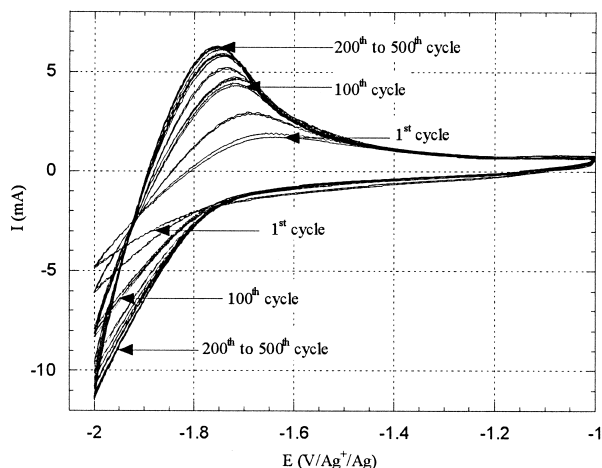


Fig. 2. Cyclic voltammety of the n-doping of PFPT enclosed in aluminium grid. 500 cycles. Sweep rate: 20 mV s^{-1} , electrolyte 1 M NEt_4^+ , CF_3SO_3^- in acetonitrile.

cycles were reached without loss of capacity. This is one of the first published experiments to report such a cyclability from this chemically prepared polymer in its n-doping domain.

From Fig. 2, it can be observed that the process improves during the first 200 cycles and then stabilizes. This may be explained by the unbound structure of the electrode with the electronic percolation inside the electrode reaching its maximum after 200 cycles.

Fig. 3 shows the cyclic voltammogram of a PFPT/electronic conductor mixture, bound onto a grid of expanded aluminium with CMC. The composition of the electrode was 60% conductor, 30% PFPT and 10% CMC. The electronically conducting material used was acetylene black which has a small capacitive behaviour (this can be seen on Fig. 3, where the polymer is in its isolating state, i.e.,

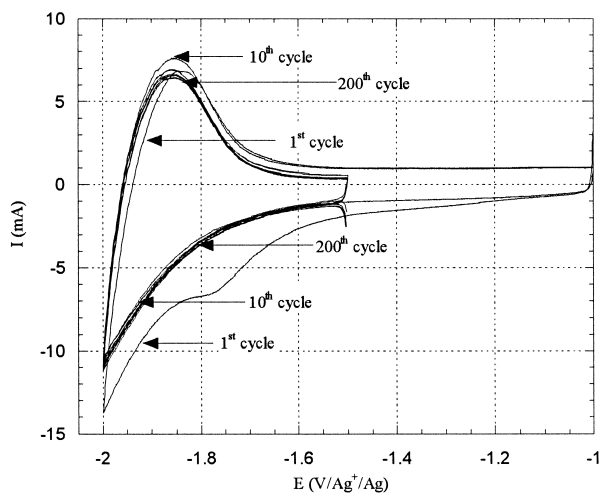


Fig. 3. Cyclic voltammety of the n-doping of PFPT bound with 10% CMC on a 4 cm^2 aluminium grid. 200 cycles, Sweep rate: 20 mV s^{-1} , electrolyte 1 M NEt_4^+ , CH_3SO_3^- in acetonitrile. The electrode contained 3 mg of PFPT.

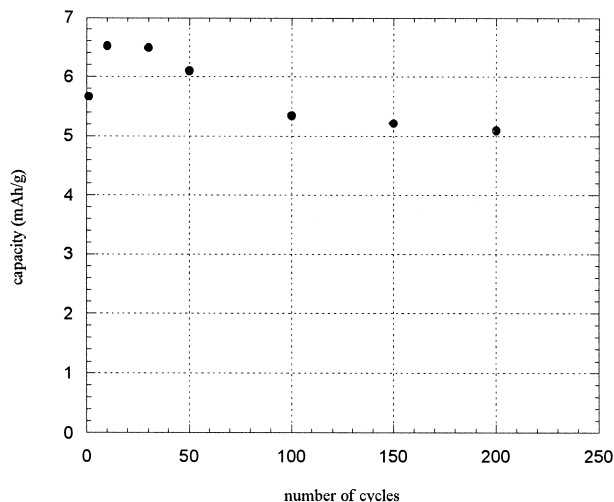


Fig. 4. Partial capacity of PFPT during the cycling performed in Fig. 3.

$E \geq -1.5 \text{ V/ref}$). The first 10 cycles represent the activation step of the polymer: during these cycles, the polymer doping process decreases while the polymer undoping process increases. It means that the charge-trapping phenomenon (ions inserted and irreversibly trapped in the polymer chains) is important in the first cycles and then decreases with cycling. During cycling, an equilibrium establishes between the doping and undoping processes and more than 80% of reversibility is reached at the end of this activation step.

Fig. 4 represents the loss of the discharged capacity with cyclings. After 200 cycles, the loss of capacity was 22%. For this experiment, the counter electrode was a 4 cm^2 platinum foil and thus the undoping decrease can be attributed to the electrolyte oxidation on the Pt electrode.

Fig. 5 shows the Pth positive doping process. The polymer is p-undoping from 0.7 V/ref to 0 V/ref . The

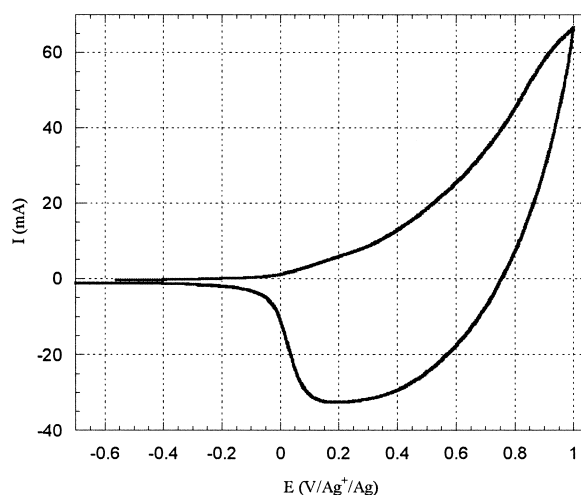


Fig. 5. Cyclic voltammety of the p-doping of Pth bound with 10% CMC on a 4 cm^2 stainless steel grid. Sweep rate: 20 mV s^{-1} , electrolyte 1 M NEt_4^+ , CF_3SO_3^- in acetonitrile.

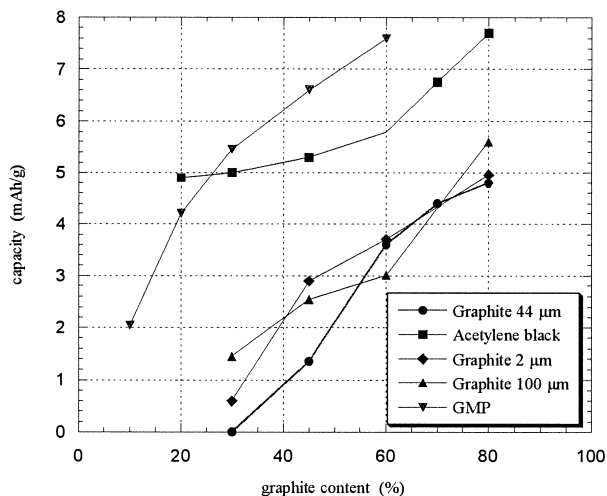


Fig. 6. Partial capacity of PFPT with different electronically conducting additives, measured during cyclic voltammetry at 20 mV s^{-1} to -2 V/ref .

activation step is around 10 cycles, as with PFPT. The specific capacity reached 40 mAh g^{-1} of polymer.

3.3. Electrode composition

3.3.1. Study of electronic conduction

In the previous experiments, the electrode composition was 60% graphite ($44 \mu\text{m}$), 30% polymer and 10% CMC. The amount of graphite needed, to ensure a good electronic conduction in the electrode when the polymer is in its isolating state, can be considered as a dead mass in terms of specific capacity of the electrode. It is therefore necessary to minimize the graphite content in the electrode. In this study, different conducting additives were tested at various percentages in the electrode in order to increase the polymer/conductor ratio, taking into account the specific capacitance of the polymer, obtained by cyclic voltammetry.

Fig. 6 presents the capacity of PFPT with different electronically conducting additives and at various amounts in the electrode (all compositions with 10% CMC). Measurements were made after 10 cycles of cyclic voltammetry to -2 V/ref at 20 mV s^{-1} , and are thus only partial undoping capacities.

Several electronically conducting additives were tested: spherical graphites of different sizes ($2 \mu\text{m}$, $44 \mu\text{m}$, $100 \mu\text{m}$), GMP graphite (not industrially available), and acetylene black (AB). As can be seen on Fig. 6, AB and GMP seem to be more efficient than spherical graphites. It can be explained by their structures conferring a better ability to conduct the current between the polymer chains: GMP is a disc-shaped graphite and AB has a fibrous structure. The use of these two conducting additives allowed us to decrease the conductor content, while keeping the specific capacity higher than 5 mAh g^{-1} of polymer. It was decided to use AB as electronic conductor in the electrode, due to its industrial production.

3.3.2. Binder study

Three types of binder were tested: PVDF, CMC and PTFE.

Figs. 7 and 8 show the doping processes of PFPT and PTh when bound with each binder. PVDF and PTFE were used with an electrode content of 5% in weight and CMC with a content of 10%, which is the minimum percentage to give some mechanical strength.

The electrodes bound with PVDF and PTFE exhibited a strong resistive behaviour in the positive domain and the Pth p-doping was very poor. These results show that PVDF and PTFE seem to isolate the active materials from the current collector or to prevent the insertion of ions into the polymer chains. Thus, they appear not to be good binders for positive electrodes.

For the negative electrode, both PVDF and PTFE allowed good doping of the polymer, but the doping process did not have a good coulombic reversibility. This can be explained by a charge-trapping phenomenon or a parasitic reaction with the binders. Nevertheless, both binders confer good mechanical properties to the electrode.

CMC has been used in a proportion of 10 wt.% and seems to maintain the electrochemical properties of the polymers. However, with this content of binder the mechanical properties of the electrode were very poor. Also, CMC cannot be used at more than 40°C if the electrolyte system is not absolutely anhydrous and deoxygenated.

Fig. 9 presents the cyclic voltammogram of the PFPT n-doping obtained with two different binders: CMC (the best result reached), and a new binder (referenced as 'A'). It can be pointed out that binder A allows a very good doping of the polymer, with an excellent coulombic reversibility (more than 90%). Partial capacities obtained were 3.7 mAh g^{-1} of PFPT for the electrode bound with CMC and 5.9 mAh g^{-1} for the electrode bound with A.

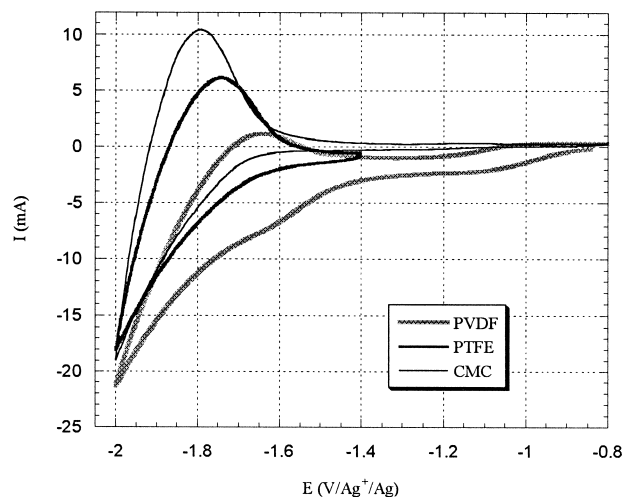


Fig. 7. N-doping of PFPT for different binders. Sweep rate: 20 mV s^{-1} . 9 mg of PFPT, graphite 60%, electrolyte 1 M NEt_4^+ , CF_3SO_3^- in acetonitrile.

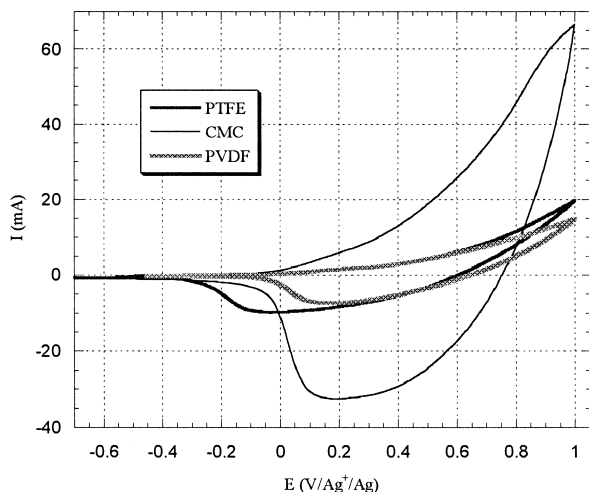


Fig. 8. P-doping of Pth for different binders. Sweep rate: 20 mV s^{-1} . 11 mg of Pth, graphite 60%, electrolyte 1 M NEt_4^+ , CF_3SO_3^- in acetonitrile.

As this was an efficient way of binding polymers, tests were performed to decrease the amount of conductive additive used with this binder.

Fig. 10 presents the cyclic voltammograms of PFPT with different electrode compositions. It can be seen that a AB/PFPT mass ratio of 65/30 (= 0.46) confers a good conductivity inside the electrode with a good capacity from the polymer. With the other electrode compositions (more polymer and less electronic conductor), the resistance inside the electrode was higher and the specific capacity of the polymer was decreased.

It can be concluded that a minimum AB/PFPT ratio in weight of 0.46 is needed with this binder to obtain a good electronic percolation in the electrode and good electrochemical properties for the polymer.

The best electrode composition selected was 65% polymer, 30% acetylene black, 5% binder A.

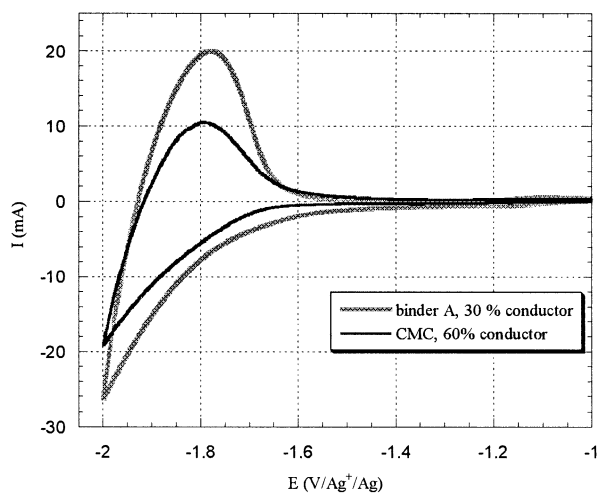


Fig. 9. Cyclic voltammograms of the n-doping of PFPT, Sweep rate: 20 mV s^{-1} . Using aluminium grid collectors and different binders, electrolyte 1 M NEt_4^+ , CF_3SO_3^- in acetonitrile.

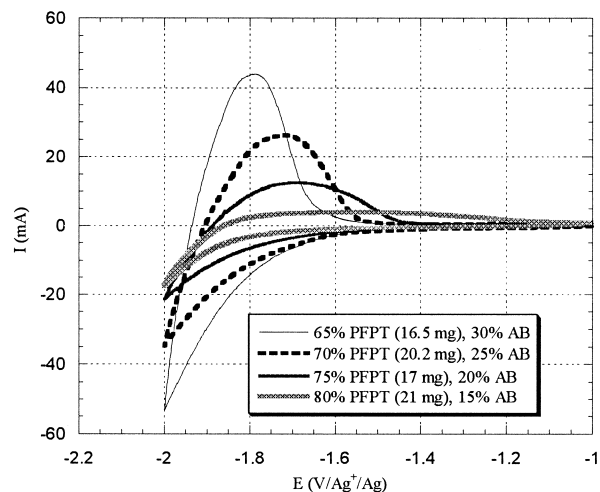


Fig. 10. Cyclic voltammograms of the n-doping PFPT of bound onto a 4 cm^2 aluminium grid with 5% of binder A. Sweep rate: 20 mV s^{-1} , different electrode compositions, electrolyte 1 M NEt_4^+ , CF_3SO_3^- in acetonitrile.

3.4. Supercapacitors

Systems using PFPT as the negative electrode and Pth as positive electrode have been built. The electrolyte was the same as the one used for electrochemical characterization: 1 M NEt_4^+ , CF_3SO_3^- in acetonitrile. A cellulosic separator (2 pieces, each $100 \mu\text{m}$ thick) was used to electronically isolate the electrodes.

Fig. 11 shows the galvanostatic charge and discharge of such a system. The current collectors were 4 cm^2 expanded grids of stainless steel, and the electrode composition was 30% PFPT, 60% $44 \mu\text{m}$ graphite and 10% CMC. Charges and discharges were performed at a current density of 2.5 mA cm^{-2} . It is pointed out that the system cycles between 2.3 and 3 V. These curves led to specific capacities of 260 F g^{-1} for Pth and 110 F g^{-1} for PFPT.

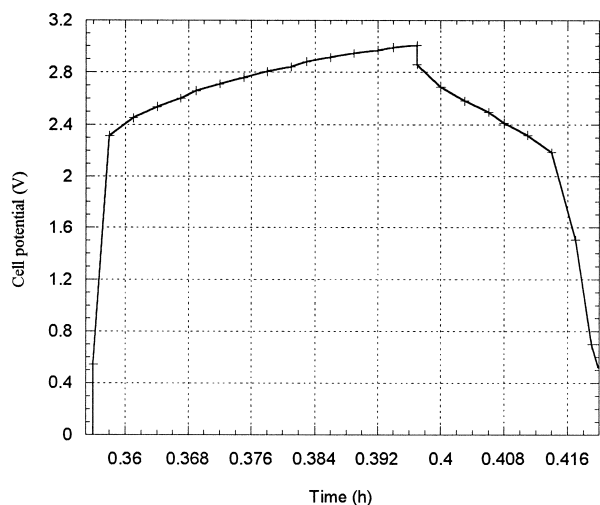


Fig. 11. Galvanostatic cycling of the supercapacitor: at a charge/discharge rate of 10 mA . Electrolyte 1 M NEt_4^+ , CF_3SO_3^- in acetonitrile.

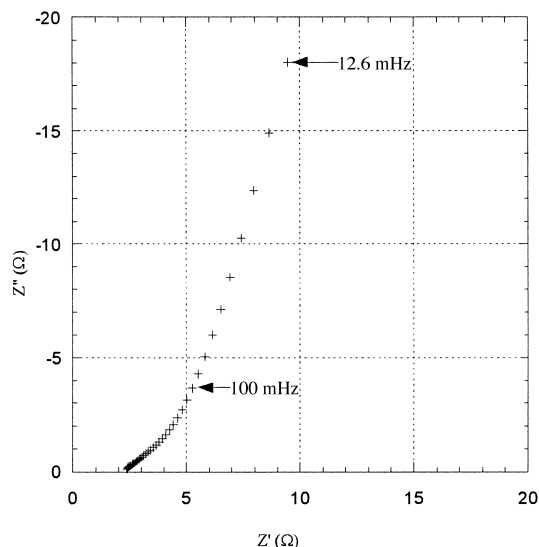


Fig. 12. Nyquist plot of the supercapacitor: PFPT//1 M $\text{NET}_4^+\text{CF}_3\text{SO}_3^-$ in acetonitrile//Pth.

Those values are approximately the same as the theoretical ones. There are still problems of cyclability for these devices. Different factors can explain this problem. One is the difficulties in getting positive and negative electrodes with the same capacity. If this condition is not fulfilled, the potential of the undercapacitive electrode goes into a potential range where electrolyte degradation can occur.

Fig. 12 presents the Nyquist plot of this supercapacitor. We can see that the internal resistance of the system is rather high (12 ohm cm^{-2} at 1000 Hz) but at low frequency, the cell behaviour is relatively close to the one obtained for a pure capacitance.

Future work will consist of the fabrication of supercapacitors using the electrode composition which has been found to be the most interesting: 65% polymer, 30% acetylene black and 5% binder A.

4. Conclusions

Chemical synthesis of polythiophene and poly-4-fluorophenylthiophene have been performed with good yields. The good electrochemical properties of these polymers have been demonstrated: 500 cycles without loss of capacity; 7 mAh g^{-1} for PFPT, 40 mAh g^{-1} for Pth were obtained during cyclic voltammetry at 20 mV s^{-1} between -2 V/ref and $+1 \text{ V/ref}$.

Studies of the electrode composition have led to the selection of acetylene black as the electronically conducting additive in the electrode and of a new binder for the active materials on the aluminium expanded grids. The best electrode composition selected was 65% polymer, 30% acetylene black, 5% binder A.

Preliminary devices have been built, showing the power capabilities of such systems. 260 F g^{-1} of Pth and 110 F g^{-1} of PFPT were obtained from un-optimized supercapacitors. Full capacity was delivered between 3 V and 2.3 V. Nevertheless, work has still to be done to decrease the internal resistance of the systems and to improve their cyclability.

Acknowledgements

We would like to thank the European Commission for its financial support within JOULE III contract number JOE3-CT97-0047 and also to CEAC-EXIDE Research Department, ENEA, Arcotronics Machinery Division and to the Dipartimento di Chimica, University of Palermo.

References

- [1] C. Arbizzani, M. Mastragostino, L. Meneghello, *Electrochim. Acta* 41 (1996) 21.
- [2] A. Rudge, I. Raistrick, S. Gottesfeld, J.P. Ferraris, *Electrochim. Acta* 39 (1994) 273.
- [3] Matsushita Electric Industrial, Japanese Patent 132.335, 1980.
- [4] Y. Kibi, T. Saito, M. Kurata, J. Tabuchi, A. Ochi, *J. Power Sources* 60 (1996) 219.
- [5] M. Sato, S. Tanaka, K. Kaeriyama, *J. Chem. Soc., Chem. Commun.* (1987) 1725.
- [6] C. Arbizzani, M. Catellani, M. Mastragostino, C. Mingazzini, *Electrochim. Acta* 40 (1995) 1876.
- [7] D.J. Guerrero, X. Ren, J.P. Ferraris, *Chem. Mater.* 6 (1994) 1437.
- [8] T. Yamamoto, K. Sanechika, A. Yamamoto, *Bull. Chem. Soc. Jpn.* 56 (1993) 1497.
- [9] J.P. Montheard, J.F. Delzant, M. Gazard, *Synthetic Communications* 14 (3) (1984) 289.
- [10] K. Tamao, S. Kodama, I. Nakajima, M. Kumada, *Tetrahedron* 38 (1982) 3354.
- [11] S. Mashida, S. Miyata, *Synthetic Metals* 31 (1989) 311.
- [12] M. Shimomura, M. Kaga, N. Nakayama, S. Miyauchi, *Synthetic Metals* 69 (1995) 313.
- [13] J.E. Österholm, J. Laakso, P. Nyholm, *Synthetic Metals* 28 (1995) 435.
- [14] T. Olinga, B. François, *Synthetic Metals* 69 (1995) 297.
- [15] V.M. Niemi, P. Knuuttila, J.E. Österholm, *Polymer* 33 (1989) 1559.