

Short communication

Poly(3-methyl thiophene)/PVDF composite as an electrode for supercapacitors

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Abstract

Composite electrodes for supercapacitors are prepared via template synthesis by the electrochemical polymerization of 3-methyl thiophene in the heterogeneous void spaces of polyvinylidene fluoride (PVDF) porous films. The large pore size distribution in the template matrix results in some of the poly(3-methyl thiophene) growing in a more ordered fashion than in films synthesized without spatial restriction, and this can lead to improved conductivity and kinetics. In this work, the capacitance properties of a poly(3-methyl thiophene)/PVDF composite were investigated using cyclic voltammetry, ac impedance spectroscopy and charge–discharge tests. The P(3-MeT)/PVDF|PC/EC/1 mol L⁻¹ LiClO₄|P(3-MeT)/PVDF type III capacitor had a specific capacitance of 616 F g⁻¹ and a Coulombic efficiency of 93%. The power density decreased during ~300 cycles and then became practically constant at 7.3 kW kg⁻¹. These results indicate that template synthesis is a useful alternative to enhance the properties of conducting polymers.

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1. Introduction

The discovery of conducting polymers has created many new possibilities for devices that combine unique optical, electrical and mechanical properties. The literature on conducting polymers, as reflected in the most cited papers, shows the diversity of materials that can be used, the optical effects achieved, and the underlying physical processes [1–4]. The potentially useful materials include organic polymers, copolymers, and conjugated polymers such as polyaniline [5], polypyrrole [6] and polythiophene [7]. Applications for these polymers have begun to emerge through the reversibility of doping, and include chemical sensing, blends for electrostatic dissipation and electromagnetic-interference shielding, electromagnetic-radiation absorbers, conductive layers for anticorrosion coatings for iron and steel, light-emitting polymer devices and energy storage (batteries and supercapacitors).

Supercapacitors are energy and power storage devices that have technical and economic advantages in a diverse range of consumer and industrial applications, including electric vehicles, uninterruptible power supplies, and memory protection of computer electronics and cellular communication devices [8,9]. A supercapacitor is very similar to batteries except that: (i) the electrodes used are usually identical and (ii) the charge storage in electroactive electrode materials is capacitive in origin and involves mainly the translational motion of charged species [10]. Two types of electrochemical capacitor are currently under development, namely, the electric double-layer capacitor (EDLC) and the redox- or pseudo-capacitor (PC) [11]. In the former, energy storage arises mainly from the separation of electronic and ionic charges at the interface between electrode materials with a high specific area and the electrolyte solution. In the latter, fast faradaic reactions occur in the electrode materials at characteristic potentials.

Much attention has been focused on redox electrochemical capacitors containing conducting polymers that greatly enhance the stored energy because of the faradaic processes that occur in their bulk. Thin film polymer electrodes are generally used in the energy storage device. There are three possible configurations:

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type (I) a supercapacitor with both electrodes constituted by the same p-dopable conducting polymer, type (II) a supercapacitor with two different p-dopable conducting polymer and type (III) a supercapacitor with a p- and n-dopable conducting polymer. Configuration (III) is the most favorable in terms of energy and power density. However, the complex morphology of conducting polymers plays a crucial role in their physical properties. In general, conjugation length, interchain interactions and the extent of disorder are significant parameters that govern the final characteristics of the resulting polymer [12]. Although preferential couplings during the polymerization of pyrroles and thiophenes occur at positions 2 and 5, secondary reactions are possible at positions 3 and/or 4, leading to branched products. Indeed, the possibility of controlling the electronic and optical properties of a conducting polymer by tailoring the organic molecular structure (precluding structural defects) will open new possibilities for using these materials in technological applications.

One of the most promising alternatives for producing conductive polymers with fewer structural defects is the encapsulation of the polymer chains in the internal cavities of host structures. Among the possibilities for obtaining encapsulated polymers, the “template synthesis” of conducting polymers in cavities, pores and lamellae has been explored to produce highly ordered polymer chains with optimized characteristics. In this technique, materials can be deposited within the void spaces of the host materials. These void spaces act as a template that determines the shape, size and, in many cases, the orientation of the particle produced. Hence, by synthesizing conducting polymers in a confined medium, the polymer chains are forced to align within the environment of the host matrix and an enhanced conductivity can be expected. When the host matrix is not dissolute, a composite is obtained.

Polymers grown by chemical or electrochemical methods from the substrate/host material can completely or partially fill the interstitial space within the host material. The presence of pores not filled by conducting polymer may improve its electrochemical properties by enhancing the mass transport of counter ions associated with the doping process [13–15].

Research into polymer-intercalated composites is not exclusively directed towards obtaining high-conductivity materials. Other important properties could also be of interest for a variety of applications. The purpose of this work was to investigate the effects of template synthesis on the use of a poly(3-methyl thiophene)/PVDF composite film as an electrode in supercapacitors.

2. Experimental

2.1. Preparation of PVDF membranes

PVDF membranes were used as templates for polymer synthesis. 8% (w/w) PVDF (Aldrich) solutions in dimethylacetamide (DMA, Merck) were spin-coated at room temperature on ITO glass. Phase separation was done by immediate immersion in a non-solvent bath (acetone:methanol, 1:1, v/v). The thickness of the porous film was about 20 μm .

2.2. Template synthesis of poly(3-methyl thiophene)—P(3-MeT)

The polymerization of P(3-MeT) inside the porous films was done using the galvanostatic mode by applying a current density of $10 \mu\text{A cm}^{-2}$ with a three-electrode set-up. The working electrode consisted of an ITO glass coated with PVDF film, while lithium plates served as counter and reference electrodes. The electrolyte consisted of 0.01 mol L^{-1} KBF_4 (Aldrich) containing 0.1 mol L^{-1} of distilled 3-methyl thiophene (Aldrich) in propylene carbonate (PC). The synthesis was done at room temperature under an argon atmosphere in a dry box. The poly(3-methyl thiophene) mass in the composite, as calculated from the deposition charge [16] ($Q_{\text{oxidation}} = 10 \text{ mC cm}^{-2}$), was $10.08 \mu\text{g}$.

2.3. Scanning electron microscopy

Scanning electron microscopy was done using a JEOL model JSM-5900LV scanning electron microscope after coating the sample films with gold by sputtering in a Bal-tec sputter-coater (SCD 50 model).

2.4. Electrochemical characterization of the P(3-MeT)/PVDF composite

Cyclic voltammetry, electrochemical impedance spectroscopy and chronopotentiometry measurements were done with a P(3-MeT)/PVDF| 1.0 mol L^{-1} LiClO_4 PC-EC 1:1|Li system, where EC is the solvent ethylene carbonate. Impedance spectra were recorded by applying an ac amplitude of 10 mV and the data were collected in the frequency range of 10^5 – 10^{-2} Hz. The impedance data were analyzed using Boukamp's fitting program [17,18]. All electrochemical data were obtained with an AUTOLAB-PGSTAT30 potentiostat.

2.5. Electrochemical characterization of the capacitor

The electrochemical capacitor was characterized using a P(3-MeT)/PVDF| 1.0 mol L^{-1} LiClO_4 PC-EC 1:1|P(3-MeT)/PVDF system configuration. The capacitor performance was characterized based on galvanostatic charge–discharge tests and impedance measurements.

3. Results and discussion

The microstructure of the PVDF membrane film used as the template matrix is shown in Fig. 1. The large size pore distribution (~ 2.5 – 800 nm [14]) in the template matrix resulted in some of the poly(3-methyl thiophene) growing in a more ordered fashion than in films synthesized without a spatial restriction.

The inset in Fig. 2 shows a chronopotentiometric curve for template synthesis done in a dry box because poly(3-methyl thiophene) is easily degraded in the presence of oxygen. The potential increased until 4.5 V versus Li then, remained constant (oxidation charge = 5 mC cm^{-2}). The color of the porous films changed from white (PVDF) to blue after formation of the composite. This is the typical color of the oxidized form of P(3-

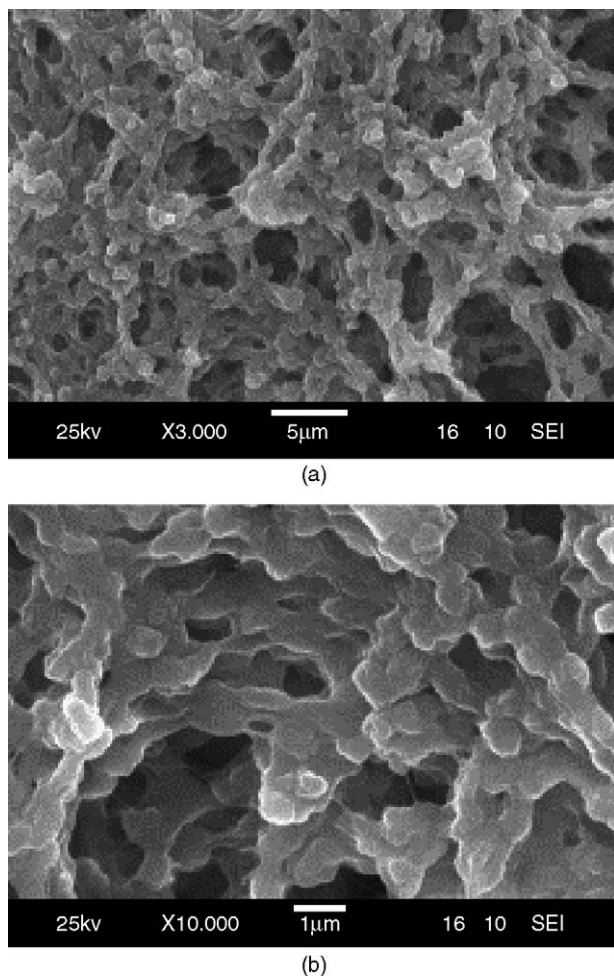


Fig. 1. Scanning electron micrographs of PVDF template membrane at two magnifications: (a) 3,000 \times and (b) 10,000 \times .

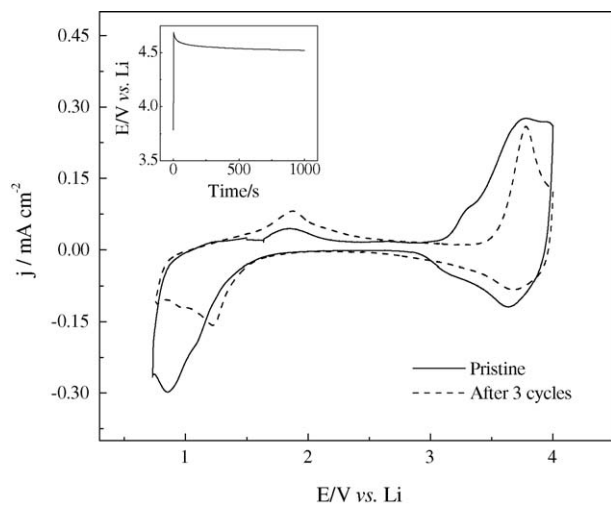


Fig. 2. Cyclic voltammetry of the P(3-MeT)/PVDF/PC/EC/1 mol L⁻¹ LiClO₄/Li system at 10 mV s⁻¹. Inset: the chronopotentiometric curve of the composite synthesis; $j = 10.0 \mu\text{A cm}^{-2}$.

MeT) and indicated the formation of a polymer within the void spaces of the template matrix.

Fig. 2 shows the cyclic voltammetry curves recorded on a poly(3-MeT)/PVDF composite film. Steady-state conditions were reached from the third cycle onwards. A well-developed cathodic–anodic peak system was visible in the potential range between 0.75 and 2.30 V versus Li. The reduction wave at 1.22 V corresponded to the injection of electrons into the conducting polymer and to the insertion of cations from the electrolyte into the electrode to preserve the electroneutrality. This led to a change in the electronic structure of the polymer to make it electronically conductive. The undoping process appeared as an oxidation wave on the reverse scan, at 1.87 V, and represented electron extraction from the polymer and the removal of cations. The polymer subsequently returned to its neutral and isolating state. This redox process is also known as poly(3-MeT) n-doping.

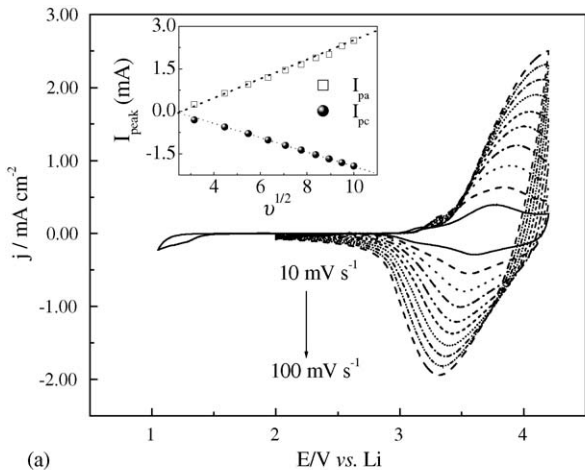
The same process of ion insertion occurred in the potential range from 3.20 to 4.00 V, with the electrons now being extracted from the polymer and the anions being inserted from the electrolyte into the polymer. The p-doping of the P(3-MeT)/PVDF film appeared as an oxidation wave at 3.78 V and the undoping as a reduction peak at 3.67 V. Anions were removed while electrons were injected into the polymer. The same behavior was observed by H. Ding [19] when TBAPF₆ was used as a support. Our observation of n-doping in LiClO₄ medium may indicate that the spatial restraint in the PVDF matrix was sufficient to induce the formation of more ordered poly(3-methyl thiophene) chains in this composite, thereby improving its electrochemical properties. The observation of p- and n-doping from a P(3-MeT)/PVDF composite film was very interesting because it suggested the possibility of obtaining a III type supercapacitor. In terms of energy and power density, these supercapacitors are the most favorable type for electrochemical applications. The system stabilized after three voltammetric cycles, with a decrease in the total charge capacity of about 30%.

The electrodes modified with composite showed defined oxidation and reduction current peaks at several sweep rates for both p- and n-doping process (Fig. 3a and b).

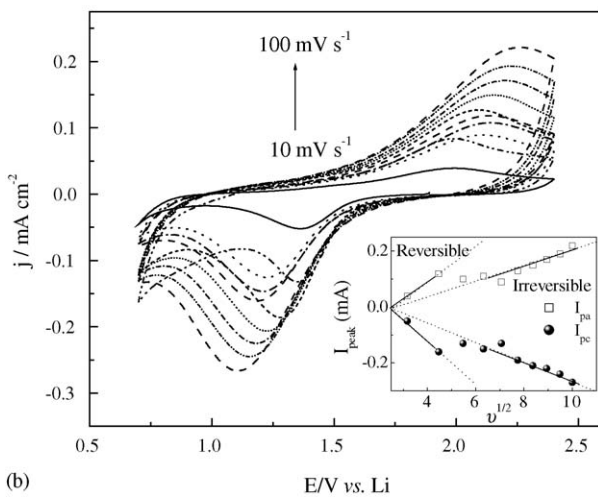
A test of the reversibility of the system was to check whether a plot of I_p as a function of $v^{1/2}$ was linear and passed through the origin. Reversible behavior was observed only for the p-doping process (Fig. 3a). A reversible cyclic voltammogram is generally only observed if both the oxidized and reduced species are stable and the kinetic of the electron transfer process is fast. This fast kinetics may be related to template synthesis, which decreases the defects along the poly(3-methyl thiophene) chain, thereby improving the electronic and ionic conductivity. The diffusion coefficient was determined using the Randles–Sevcik equation [20]. The values obtained for the anodic and cathodic current peaks were very similar ($1.2 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ and $9.1 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$, respectively).

In the case of n-doping the irreversible behavior was verified in Fig. 3b, which the inset shows the transition from reversible to irreversible behavior with increase of the sweep rate.

Plots of the discharge capacitance of the P(3-MeT)/PVDF composite electrode calculated from cyclic voltammograms



(a)



(b)

Fig. 3. Cyclic voltammetry of the P(3-MeT)/PVDF|PC/EC/1 mol L⁻¹ LiClO₄|Li system at several scan rates for (a) p-doping and (b) n-doping. Inset shows a plot of the dependence of the peak current density on the square root of the potential sweep rate.

showed the influence of sweep rate on the electrochemical performance of the capacitor (Fig. 4).

The discharge capacitance decreased significantly with increasing scan rate up to 40 mV s⁻¹, mainly because the resistance in the system caused a delay in the time required to discharge the capacitor. In the P(3-MeT)/PVDF composite electrode, the resistance can be related to two main factors, namely, the transition of the conducting polymer to an isolated state during the discharge process and the isolating capacity of the template matrix (PVDF porous film). The exact time required to discharge the capacitor depends on the resistance (R) and the capacitance (C) in the discharging system, as expressed by the relationship:

$$T_C = RC \quad (1)$$

where T_C is the capacitive time constant (s), R is the resistance (Ω) and C is the capacitance (F).

However, from 40 mV s⁻¹ on, the decrease in the specific discharge capacitance was not so pronounced with increasing sweep rate. Once more, template synthesis was responsible for

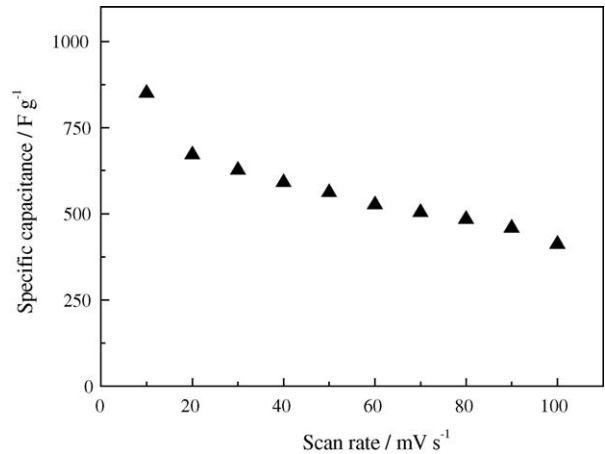


Fig. 4. Specific discharge capacitance of the P(3-MeT)/PVDF composite electrode as a function of sweep rate.

this behavior, with the porous structure of the composite allowing a higher swelling of P(3-MeT) by the electrolyte solution and the formation of parallel ionic and electronic conduction paths. This phenomenon also contributed to maintain the capacitive property of the composite, despite the increase in scan rate.

The charge–discharge properties of a P(3-MeT)/PVDF|PC/EC/1 mol L⁻¹ LiClO₄|P(3-MeT)/PVDF system were evaluated in order to demonstrate the electrochemical performance of these composite electrodes in a capacitor with a type III configuration. In this measurement, one electrode was kept in the oxidized state and another in the reduced state. The typical charge–discharge characteristics of the cell are illustrated in Fig. 5. For fully-charged and -discharged states of the cell, the contribution of p- and n-doping must be considered.

The discharge capacitance C was evaluated from the linear part of the discharge curves using the relationship:

$$C = i \frac{\Delta t}{\Delta V} \quad (2)$$

where i is the constant current and Δt is the time interval for the change in voltage ΔV . The Coulombic efficiency, η , was

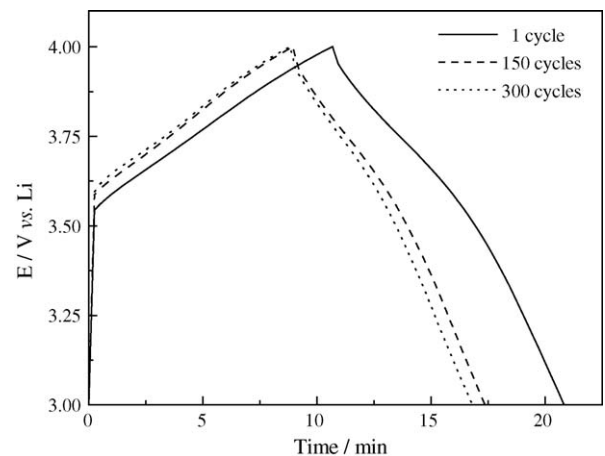


Fig. 5. Galvanostatic charge–discharge characteristics of P(3-MeT)/PVDF|PC/EC/1 mol L⁻¹ LiClO₄|P(3-MeT)/PVDF; $j = \pm 10 \mu\text{A cm}^{-2}$.

Table 1
Characteristics of the P(3-MeT)/PVDF|PC/EC/1 mol L⁻¹ LiClO₄|P(3-MeT)/PVDF capacitor

| Discharge cycles | Specific discharge capacitance (F g ⁻¹) | Coulombic efficiency (%) | Specific power (kW kg ⁻¹) |
|------------------|---|--------------------------|---------------------------------------|
| 1 | 616 | 93 | 9.3 |
| 150 | 514 | 91 | 7.6 |
| 300 | 491 | 89 | 7.3 |

calculated using Eq. (3) with the same current used for charging and discharging:

$$\eta = \frac{t_D}{t_C} \times 100\% \quad (3)$$

where t_D and t_C are the times for discharging and charging, respectively.

The characteristics of the type III capacitor are reported in Table 1.

Initially, the system delivered a specific capacitance of 616 F g⁻¹, which was calculated based only on the mass of the active material participating in the electrochemical reaction ($m_{P(3-MeT)} = 10.08 \mu\text{g}$). After 150 cycles, there was a decrease in the specific capacitance of about 16%, after which the capacitance remained practically constant. The Coulombic efficiency of the capacitor over 1–300 cycles was between 93 and 89%. The P(3-MeT)/PVDF composite reached specific power values of approximately 7.3 kW kg⁻¹ after 300 cycles, under low current density (10 $\mu\text{A cm}^{-2}$). These results were considered promising because: (i) they were similar to the values reported for the hydrous form of ruthenium oxide, which is the best example of the inorganic class of pseudocapacitive materials [21–23] and (ii) they were better than those for conducting polymers, which normally can reach specific capacitance values of approximately

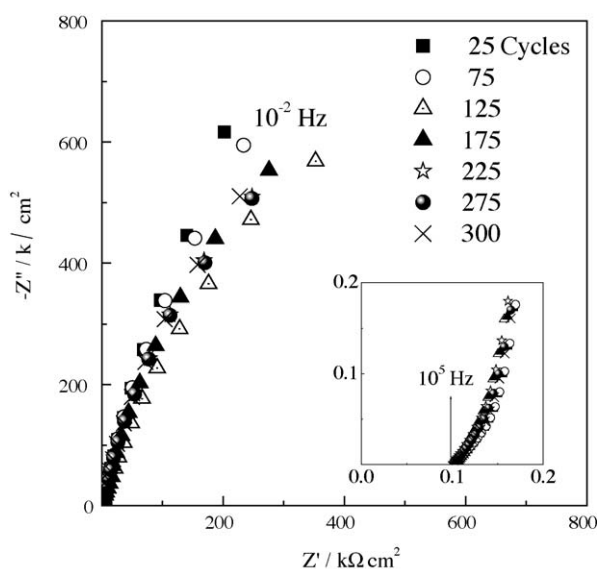


Fig. 6. Nyquist diagram of the P(3-MeT)/PVDF|PC/EC/1 mol L⁻¹ LiClO₄|P(3-MeT)/PVDF system at OCP. Perturbation amplitude 0.01 V and frequency range from 10⁵ to 10⁻² Hz.

400–500 F g⁻¹ with a specific power of more than 2 kW kg⁻¹ [24–26].

Fig. 6 shows the electrochemical impedance data for the electrochemical capacitor at open circuit potential during 300 charge/discharge cycles.

The behavior is typical of a capacitor in which there is no high frequency semicircle related to a charge transfer process and the impedance starts from a diffusion process (Warburg diffusion). This fact can again be related to template synthesis, which organizes the chain polymer and increases the conductivity of P(3-MeT). At low frequency range, only the imaginary part increased with decreasing frequency, as a result of the capacitive response. The impedance remained practically constant after 300 cycles, indicating that the system had stabilized and that there was no degradation with the cycling.

4. Conclusions

A P(3-MeT)/PVDF composite was prepared by template synthesis. Using this approach, the concentration of defects in the poly(3-methyl thiophene) chains decreased and made it possible to achieve p- and n-doping in the composite, a very important feature for electrode material in type III supercapacitors. The electrodes showed fast, reversible kinetics for p-doping, with a diffusion coefficient of $\approx 1.2 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$. The specific capacitance was 616 F g⁻¹. After 150 cycles, there was a decrease in the specific capacitance of the system of about 16%. The Coulombic efficiency of the capacitor over 1–300 cycles was between 93 and 89%. The impedance remained practically constant after 300 cycles, indicating that the system was stable and did not degrade with the cycling.

The promising results obtained here can be attributed to template synthesis of the conducting polymer. The formation of a continuous conducting network within the porous PVDF matrix increased the electroactive surface area exposed to the electrolyte, thereby providing parallel ionic and electronic conduction pathways that improved the process of charge transfer and mass transport. The balance between these processes was responsible for the good performance of the type III capacitor using a P(3-MeT)/PVDF composite as electrodes.

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