

Morphological and electrochemical characterization of a poly(3-methylthiophene)/PVDF composite

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Abstract

Composite electrodes were prepared via electrochemical polymerization of 3-methylthiophene in porous PVDF membranes of various thicknesses. The electrochemical properties were determined by cyclic voltammetry and charge–discharge tests and the possible correlation of the results with the morphology of the host membranes was examined. The best definition of n- and p-doping/undoping processes and the biggest capacitance (82 F g^{-1}) were obtained with a $27.5 \text{ }\mu\text{m}$ -thick composite. Further characterization of this composite using electrochemical impedance spectroscopy revealed three behaviors associated with variation in the oxidation state of poly(3-methylthiophene) during transition from the n-undoping to p-doping states. The behavior of the charge transfer resistance and the double layer capacitance as a function of the applied potential were also determined.

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1. Introduction

Conducting polymers represent an interesting class of electrode materials for redox supercapacitors because the kinetics of the electrochemical charge–discharge processes, known as doping–undoping, are generally fast, with the charge being stored throughout the volume of the material. In addition, these polymers can be produced more cheaply than noble metal oxides, which have also been proposed for use in redox supercapacitors.

Once formed, the conducting 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 a high electronic conductivity. Reducing the p-doped polymer generates the ‘undoped’ state that is usually insulated or semi-insulated, depending on the degree of completion of the undoping process. For a limited number of polymers, primarily polyacetylene [1,2], poly-*p*-phenylene [3,4] and polythiophenes [4–7], electrochemical reduction of

the undoped polymer is also possible in a suitably stable environment, leading to the reduced, ‘n-doped’ state, which is also associated with a significant electronic conductivity.

Based on the nature of the charge/discharge process, three possible schemes have been proposed by Rudge et al. [8] in which the conducting polymers can be used in redox supercapacitors. In Type I capacitors, two electrodes comprising symmetrical and identical p-dopable conducting polymers are used, whereas two different p-dopable conducting polymers are used in Type II capacitors. In Type III capacitors, a configuration of n- and p-dopable polymers can be used. The classification of different types of redox capacitors is based on the potential range in which they operate. Configuration III is the most promising in terms of energy and power density, but its advantages are offset by the difficulty in obtaining polymers that can be efficiently n-doped.

Although the analogy to semiconductors is not perfect, the process of electrooxidation or electroreduction of the non-conducting state of these polymers generates mobile electronic charge carriers in the material, which explains why these charging processes can be referred to as chemical doping. Charge neutrality always has to be maintained by the appropriate exchange of an ionic charge with the electrolytic solution,

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and this requires that a conducting polymer film of high charge/discharge activity should have good electronic and ionic conductivities. The mobility of the ‘free’ electronic charges in conducting polymers depends on structural defects present in the chain backbone. For this reason, the production of polymers with optimized values of electrical conductivity is directly related to the increase in carrier mobility.

One of the most promising alternatives for producing conducting polymers with fewer structural defects is the encapsulation of polymeric chains in the internal cavities of host structures. Among the possibilities for achieving encapsulated polymers, the “template synthesis” of conducting polymers in cavities, pores and lamellae has been explored to produce highly ordered polymeric chains with optimized characteristics [9,10]. When the host matrix is not dissolved, a composite is produced.

In previous work [11], we explored the possibility of using the heterogeneous porosity of poly(vinylidene fluoride) (PVDF) membranes as a template for preparing poly(3-methylthiophene) (P(3-MeT)) composites. The wide range of void space sizes in the matrix resulted in a fraction of the poly(3-methylthiophene) growing in a more ordered fashion than in films synthesized without spatial restriction. The composites were used as electrodes in a Type III capacitor, which presented a specific capacitance of 616 F g^{-1} . The promising results have motivated to pursue the investigation in more details. Then, in this work the influence of template synthesis conditions on the electrochemical behavior of the P(3-MeT)/PVDF composite, particularly in the n-doped state of P(3-MeT), was studied. The main focus was correlated the thickness and morphology variations of PVDF matrices in the composites with the electrochemical performance determined by cyclic voltammetry, charge–discharge tests and electrochemical impedance spectroscopy.

2. Experimental

2.1. Preparation of PVDF membranes

PVDF membranes were used as templates for polymer synthesis. PVDF (Aldrich) solutions (8%, w/w, in dimethylacetamide, DMA; Merck) were spin-coated at room temperature onto 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 varied by changing the spin-coating conditions. The thickness of each membrane was determined with a profilometer (Alpha Step 200 Tencor).

2.2. Template synthesis of P(3-MeT)/PVDF composite

The polymerization of P(3-MeT) inside the porous films was done using the galvanostatic mode by applying a current density of $100 \mu\text{A cm}^{-2}/500 \text{ s}$ with a three-electrode setup. 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 $0.01 \text{ mol L}^{-1} \text{ KF}_4\text{B}$ (Aldrich) containing 0.1 mol L^{-1} of distilled 3-methylthiophene (Aldrich) in

propylene carbonate (PC). The synthesis was done at room temperature under an argon atmosphere in a dry box. The poly(3-methylthiophene) mass in the composite, as calculated from the deposition charge [12] ($Q_{\text{oxidation}} = 50 \text{ mC cm}^{-2}$), was $51 \mu\text{g}$.

2.3. Synthesis of poly(3-methylthiophene)

The polymerization of P(3-MeT) was done under the same conditions as described above, directly onto ITO substrates, to evaluate the influence of the spatial restriction imposed by template synthesis.

2.4. 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). To obtain cross-section images the PVDF membrane was unstuck of the ITO substrate and fractured into liquid N_2 .

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

Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and chronopotentiometry measurements were done with a P(3-MeT)/PVDF| $1.0 \text{ mol L}^{-1} \text{ LiClO}_4$ 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 to 10^{-2} Hz . All electrochemical data were obtained with an AUTOLAB-PGSTAT30 potentiostat.

3. Results and discussion

Fig. 1 shows the chronopotentiogram during the galvanostatic polymerization of P(3-MeT) onto ITO substrate and in the pores of the PVDF membrane. In both cases, the potential reached a high value almost immediately and was nearly

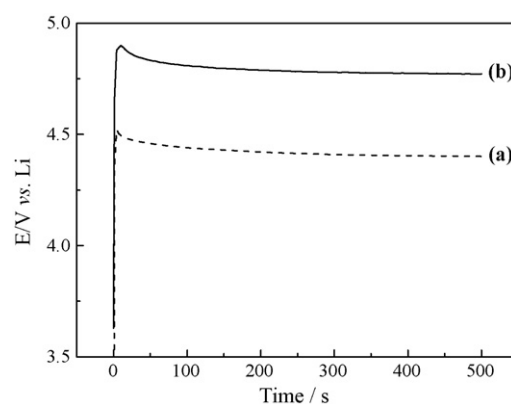


Fig. 1. Typical chronopotentiogram obtained during the galvanostatic polymerization of MeT on (a) ITO substrate and (b) inside the empty pores of PVDF membranes. The current density was $100 \mu\text{A cm}^{-2}$ in PC with $0.01 \text{ mol L}^{-1} \text{ KF}_4\text{B}$.

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