

Short communication

A novel galvanostatic polymerization for high specific capacitance poly(3-methylthiophene) in ionic liquid

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Received 12 June 2006; accepted 16 June 2006

Available online 9 August 2006

Abstract

For the first time it is here reported a novel and clean galvanostatic procedure to polymerize poly(3-methylthiophene) in the 1-ethyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl)imide (EMITFSI) ionic liquid (IL). The strategy consists in the use of the acid additive trifluoromethanesulfonimide (HTFSI) displaying the same anion of the IL and which provides an acid proton that is reduced to H₂ at the counter electrode upon the anodic polymer growth on the working electrode and prevents consumption of the ionic liquid with great advantage in terms of costs. This procedure provides a pMeT electrode featuring 250 F g⁻¹ in EMITFSI at 60 °C, a very interesting result in view of application of such pMeT in IL-based hybrid supercapacitors. Here are reported the results of the galvanostatic polymerization of pMeT in EMITFSI–HTFSI as well as the performance in EMITFSI at 60 °C of the obtained pMeT electrode.

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Keywords: Poly(3-methylthiophene); Galvanostatic electropolymerization; Supercapacitor; Ionic liquid

1. Introduction

Supercapacitors of high specific power and energy play a crucial role in the development of electric and hybrid vehicles, where they may provide the required power peaks during acceleration and energy recovery during braking [1]. The typical operating temperatures for such application are higher than room temperature (RT) and do not allow the use of commercially available double layer carbon supercapacitors based on low boiling point organic electrolytes such as acetonitrile as well as worse the performance of those featuring propylene carbonate (PC). The use of ionic liquids (ILs) as electrolytes for supercapacitors is a very promising strategy to increase the maximum operating voltage and hence the energy and power of these electrochemical devices at temperatures higher than RT [2–4]. The viability of ionic liquids has been already demonstrated in a hybrid supercapacitor with carbon as negative and poly(3-methylthiophene) (pMeT) as positive electrode over more than 15,000 cycles with cell voltage higher than 3.4 V at 60 °C. This very interesting result was achieved with electrode materials

which were developed for operation in conventional organic electrolytes, and that displayed high specific capacitances in PC-based electrolyte but significantly lower values in the investigated ILs [3,4].

To further increase the performance of the IL-based hybrid supercapacitor the polymer and carbon electrode materials should be properly designed in view of their use in the IL. As it concerns the conducting polymer, it has been demonstrated that electrochemical polymerization in the same IL used for capacitance tests provides high performing polymers [4,5] and in the case of pMeT a high specific capacitance value of 195 F g⁻¹ at 60 °C in IL can be obtained [4]. However, this result has been obtained by voltammetric polymerization which cannot be used for preparation of large amount of pMeT, whereas galvanostatic technique is more viable for practical applications. The main drawback with galvanostatic preparation of large quantities of polymer is the formation of by-products at the counter electrode which typically poison the polymerization bath as electropolymerization proceeds, and this is more important when cells without separate compartments for the working and counter electrodes are used. In the case of the electropolymerization in IL at the counter electrode takes place the reduction of the IL which is progressively poisoned and consumed and this is a great disadvantage given its high cost. Thus, it is necessary

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to control the cathodic reaction upon the electrochemical polymerization and we pursued the strategy of using an additive in the electrochemical polymerization bath, that can be reduced at the counter electrode without modifying the chemistry of the bath.

Here we report the results of a galvanostatic polymerization of pMeT in the 1-ethyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl)imide (EMITFSI) IL with the additive trifluoromethanesulfonimide (HTFSI) which is a strong acid displaying the same anion of the IL. The performance in EMITFSI at 60 °C of the obtained pMeT electrode is also reported and discussed.

2. Experimental

The EMITFSI (Degussa-Creavis) IL was dried over night at 100 °C under dynamic vacuum (Büchi Glass Oven B-580) and displayed 30 ppm of water checked by Karl Fisher titration (684 KF Coulometer Metrohm). The HTFSI (Aldrich) was used as received and MeT (Aldrich) was distilled before use.

The electropolymerization was carried out at RT in dry box (Ar atmosphere, TEKATOM) using a cell without separate compartments for the working and counter electrodes; the working electrode was glassy carbon (GC), the counter electrode a platinum sheet with area ca. 25 times in excess with respect to the working electrode; a silver wire was used as quasi reference electrode. The pMeT/GC electrodes were prepared galvanostatically in EMITFSI – 0.06 M HTFSI – 0.1 M MeT (stirred solution) with current density $i_p \geq 10 \text{ mA cm}^{-2}$ of working electrode area, and were galvanostatically undoped with current density $i_u = -0.25i_p$ in order to evaluate the electrochemical stoichiometry of polymerization and, thus, the amount of pMeT polymerized.

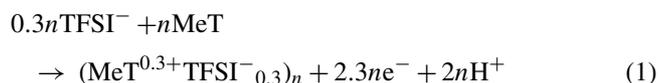
The specific capacitance of pMeT/GC was evaluated by cyclic voltammetry (CV) at 20 mV s^{-1} and 60 °C (controlled by a Thermoblock FALC oven) in dry box, using Ag quasi-reference electrode and double-layer carbon paper counter electrode with charge storage capability higher than that of the pMeT working electrode.

All the electrochemical measurements were performed with a Perkin-Elmer VMP multichannel potentiostat/galvanostat.

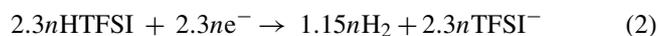
3. Results and discussion

With the aim to develop a clean galvanostatic polymerization procedure of pMeT which preserves the EMITFSI IL from contamination of by-products derived from the cathodic reaction at the counter electrode, we pursued the strategy to add in the polymerization bath the acid additive HTFSI that dissociates to give the same anion of the IL and H^+ , which in turn may give H_2 at the counter electrode while anodic polymerization takes place at the working. Hereafter are reported the anodic polymerization reaction, the expected cathodic reaction involving the HTFSI additive and the overall cell reaction upon electropolymerization, respectively; an electrochemical stoichiometry of 2.3 Faraday per mole of polymerized monomer unit (typical value for pMeT) has been considered.

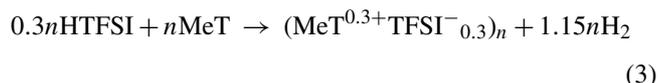
- anode reaction:



- cathode reaction:



- overall cell reaction upon polymerization:



For the overall cell reaction (3) only 0.3 mol of additive HTFSI per mole of polymerized monomer unit are required because the polymerization reaction (1) delivers 2 mol of H^+ per mole of polymerized monomer unit. Thus, the addition of HTFSI may ensure that the EMITFSI IL is neither poisoned (only p-doped pMeT and H_2 are the products) nor is consumed for the balancing of the doping charge of the polymer, and these are great expected advantages which permit to use the same EMITFSI polymerization bath for many preparations of pMeT, provided that the monomer and HTFSI are added.

This strategy is validated by the results reported in Figs. 1 and 2. Fig. 1a and b report the linear sweep voltammetry (LSV) at 20 mV s^{-1} and RT of a Pt electrode in EMITFSI and EMITFSI + HTFSI and of a glassy carbon electrode (GC) in EMITFSI + HTFSI and EMITFSI + HTFSI + MeT, respectively. In Fig. 1a the cathodic peak in EMITFSI + HTFSI at ca. -0.3 V versus Ag evidences the reduction of the acid proton of HTFSI to H_2 , and in Fig. 1b the anodic curve in EMITFSI + HTFSI + MeT indicates that monomer oxidation takes place at electrode potentials more positive than 1.2 V versus Ag, as expected for MeT. Fig. 2 reports the voltage profiles of the GC working electrode and of the Pt counter electrode upon the galvanostatic electropolymerization of pMeT at 11.3 mA cm^{-2} and the undoping

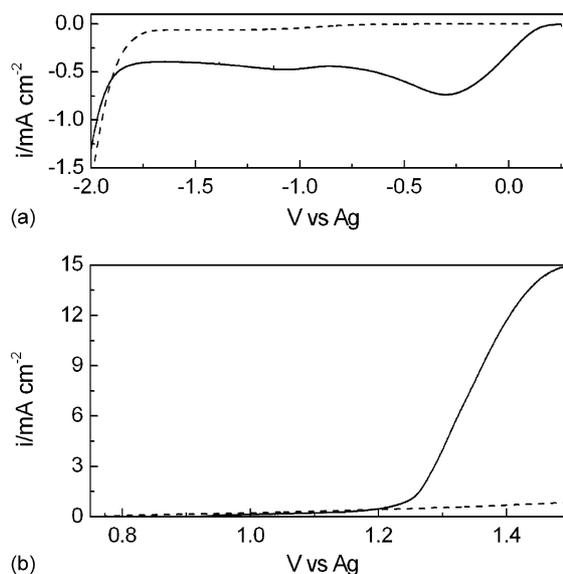


Fig. 1. LSVs at 20 mV s^{-1} and RT of (a) a Pt electrode in EMITFSI (dashed line) and EMITFSI + HTFSI (solid line) and of (b) a GC electrode in EMITFSI + HTFSI (dashed line) and in EMITFSI + HTFSI + MeT (solid line).

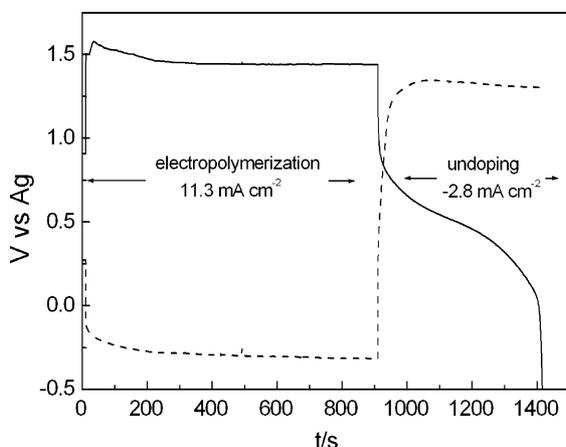


Fig. 2. Voltage profiles of the GC working electrode (solid line) and of the Pt counter electrode (dashed line) upon galvanostatic electropolymerization of pMeT in EMITFSI + HTFSI + MeT (stirred solution) at 11.3 mA cm^{-2} and undoping at -2.8 mA cm^{-2} at RT.

process at -2.8 mA cm^{-2} in EMITFSI + HTFSI + MeT at RT. Upon the growth of pMeT on the GC working electrode, which takes place at 1.5 V versus Ag, the counter electrode potential keeps stable at -0.25 V versus Ag, thus indicating that the reaction (2) is balancing reaction (1) with generation of H_2 visually observed. Upon the pMeT/GC undoping process (carried out to estimate the electrochemical stoichiometry) pMeT electropolymerizes at the Pt counter electrode. From Fig. 2 the electropolymerization and undoping charges are 10.2 and 1.4 C cm^{-2} , respectively, which give an electrochemical stoi-

chiometry of 2.32 Faraday per mole of polymerized monomer unit; thus, the pMeT loading on GC results of 4.4 mg cm^{-2} .

In view of the use of pMeT as positive electrode in IL-based hybrid supercapacitor we evaluated its specific capacitance by CV at 20 mV s^{-1} in EMITFSI at 60°C . Fig. 3a shows the voltammetric response in mA/mg of pMeT and Fig. 3b the electrode potential versus integral over time of the voltammetric current during the undoping process; from the slope of the plot reported in Fig. 3b the very high specific capacitance value of 250 F g^{-1} was evaluated. This is a very interesting value obtained with electrode sized in the typical range used for supercapacitor electrodes and prepared by an attractive procedure which can be applied for preparation of large amount of polymer. Furthermore, this datum confirms that the electrochemical polymerization in the same IL used for capacitance tests is an excellent strategy to provide a polymer of very high specific capacitance in such IL.

4. Conclusions

For the first time it is here reported a novel and clean galvanostatic polymerization of pMeT in the EMITFSI + HTFSI IL-bath in which the additive HTFSI provides the acid proton that is reduced to H_2 at the counter electrode upon the anodic polymer growth on the working electrode. Thus, the only products of the electrochemical reaction are p-doped pMeT and H_2 , and EMITFSI is not consumed with great advantage in terms of costs. This procedure provides a pMeT electrode featuring 250 F g^{-1} in EMITFSI at 60°C , a very interesting result in view of application in IL-based hybrid supercapacitors. Furthermore, such galvanostatic polymerization can be pursued to prepare electronically conducting polymers also in other ILs, provided that the corresponding acid of the IL anion is added to the polymerization bath, and working is in progress in our laboratory to polymerize pMeT in other TFSI-based ILs.

Acknowledgments

Research funded by ILHYPOS EC Project (Contract Number 518307). Degussa-Creavis is acknowledged for providing the EMITFSI IL.

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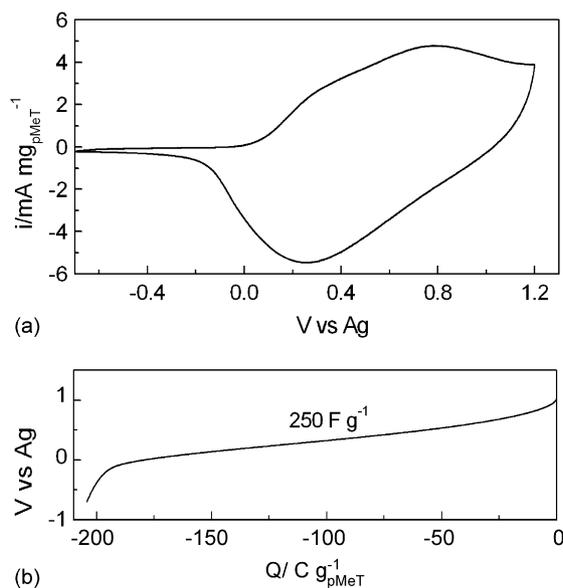


Fig. 3. (a) CV of pMeT/GC (4.4 mg cm^{-2} of pMeT) in EMITFSI at 20 mV s^{-1} and 60°C and (b) electrode potential vs. integral over time of the voltammetric current during the undoping process.