ELECTROCHEMICAL CHARACTERIZATION OF ELECTROCHEMICAL SUPERCAPACITORS BASED ON SOL-GEL SYNTHESIZED POLYPYRROLE/IRON OXIDE NANOCOMPOSITES

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Introduction

High power, energy storage electrochemical supercapacitors are attracting much interest because of their potential application in electronic devices (cellular phones, computer memory back-up, etc) and as complementary devices in electric vehicle technology [1-4]. Electronically conducting polymers are promising electrode materials for supercapacitors. They offer high charge density compared with carbons and lower cost than noble metal oxides [5,6]. In this paper we report on the synthesis of nanocomposites of polypyrrole and ion oxide by a simultaneous gelation/polymerization process, and the potential use of this materials as electrodes in redox supercapacitors.

Experimental

Nanocomposites of iron oxide and polypyrrole were prepared by a sol-gel process according to the method proposed by Suri et al. [7] using $Fe(NO_3)_3$. 9 H_2O as a precursor and 2-methoxy-ethanol as a solvent.

Composite electrodes were prepared by dry mixing followed by cold pressing (500 Kg, 5 min) the iron oxide/PPy nanocomposite, a high conductive carbon black (Super P, MMM) and PTFE as binder. PTFE concentration was keeping constant (10 wt%), while two concentrations of Super P (10 and 30 wt%) were tested. The supercapacitor cells (12 mm. diameter) were assembled from two composite electrodes that were keep apart by a glass paper separator (Whatman BS45) swollen in an 1M solution of Et_4NBF_4 in acetonitrile. Impedance measurements of the polymer and of the supercapacitors were carried out at room temperature by using the FRA module of a AUTOLAB PGSTAT30 equipment. An AC amplitude of 100 mV was used and data were collected in the frequency range of 1 MHz to 1 mH. The supercapacitor performance was evaluated by means of galvanostatic charge/discharge and cyclic voltammetry, by using a potentiostat/galvanostat AUTOLAB PGSTAT30

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Results and Discussion

The sol-gel synthesized PPy/iron oxide nanocomposites obtained are nanosized in grain size with an electrical conductivity of $1.3.10^{-7}$ $S.cm^{-1}$. Figure 1 depicts the cyclic voltammetry behaviour between 0 and 0.8V corresponding to the supercapacitor of electrode composition 80%PPy/10%SuperP/10%PTFE. It has to be noted the low current values, consequence of the low electrical conductivity of the electrode. The estimated supercapacitor capacity values ranges from a value of 1.82 mF for a sweep rate of 2 $mV.s^{-1}$ to a value of 0.13 mF at a sweep rate of 200 $mV.s^{-1}$, that corresponds to a calculated specific capacitance of 15.3 $mF.g^{-1}$ and 1.14 $mF.g^{-1}$ respectively of active material, considering that the weight of the PPy/iron oxide nanocomposite.

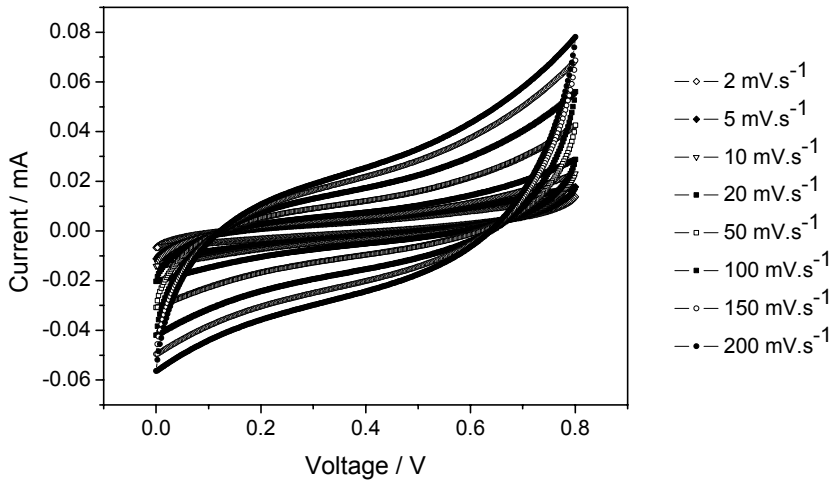

Fig. 1 *Cyclic voltammograms at different sweep rates of the symmetric 80%PPy/10%SuperP/10%PTFE supercapacitor.*

The cyclic voltametry results corresponding to the supercacitors based on 60%PPy/30%SuperP/10%PTFE electrodes displays much higher intensity values. with estimated supercapacitor capacity values ranging from 1.85 F for a sweep rate of 2 $mV.s^{-1}$ to a value of 76.6 mF at a sweep rate of 200 $mV.s^{-1}$, that corresponds to a calculated specific capacitance of 15.6 $F.g^{-1}$ and 0.64 $F.g^{-1}$. In both cases a marked degradation of the capacity behaviour was observed due to the ohmic drop.

Typical charge-discharge curves of the 60%PPy/30%SuperP/10%PTFE supercapacitor at several current densities are shown in Figure 2. For both supercapacitors the chargin time as well as discharge times decrease with increase of apparent current density, the nature of the charge-discharge curves remain unaltered during cycling, even the efficiency of charge-discharge was low. The calculated values of the specific capacitance were similar to those calculated from cyclic voltammetry experiments.

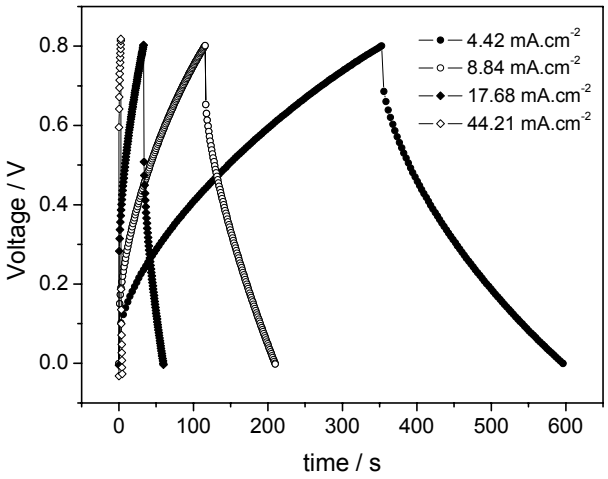

Fig. 2 *Galvanostatic charge / discharge curves for the symmetric 60%PPy/30%SuperP/10%PTFE supercapacitor at different currents densities.*

Based on the data of the charge-discharge cycling, the values of the specific power and the specific energy were calculated. The highest performance corresponds to the 60%PPy/30%SuperP/10%PTFE supercapacitor exhibiting energy densities of 1.42 Wh/Kg and power densities of 15.1 W/Kg at 2 $mV.s^{-1}$ scan rate, the maximum power density value (70 W/Kg) being obtained for a sweep rate of 50 $mV.s^{-1}$, corresponding with a energy density of 0.21 Wh/Kg.

Conclusions

Polypyrrole/iron oxide nanocomposites have been tested as electrodes in electrochemical supercapacitors. Even the results in terms of capacitance, specific energy and specific power obtained were not very satisfactory, mainly due to the high internal resistance (ESR), the sol-gel route can be consider as a promising method for the synthesis of supercapacitor electrodes.

Acknowledgements

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References

1. B.E. Conway: J. Electrochem. Soc. **138** (1991) 1539-1547.
2. B.E. Conway, V. Birss, J. Vojtowitz: J. Power Sources **66** (1997) 1-14.
3. L. Bonnefoi, P. Simon, J.F. Fauvarque, C. Sarrazin, J.F. Sarran, A. Dugast : J. Power Sources **80** (1999) 149-155.
4. M. Mastragostino, C. Arbizzani, R. Paraventi, A. Zanelli: J. Electrochem. Soc. **147** (2000) 407-412.
5. D. Bélanger, X. Ren, J. Davey, F. Uribe, S. Gottesfeld: J. Electrochem. Soc. **147** (2000) 2923-2929.
6. L. Li, D.C. Loveday, D.S.K. Mudigonda, J.P. Ferraris: J. Electrochem. Soc. **149** (2002) A1201-A1207.
7. K. Suri, S. Annapoorni, R.P. Tandon, N.C. Mehra: Synt. Met. **126** (2002) 137-143.