

High Performance Supercapacitive Behavior of Self-doped polyaniline/Manganese dioxide Nanocomposite

H.R. Ghenaatian^a, M.F. Mousavi^{a*}, M.S. Rahmanifar^b

^aDepartment of Chemistry, Tarbiat Modares University, P.O. Box 14115-175, Tehran, Iran

^bFaculty of Basic Science, Shahed University, Tehran, Iran
mfmousavi@yahoo.com, or mousavim@modares.ac.ir (M.F. Mousavi).

Abstract

Self-doped polyaniline/Manganese dioxide (SDPA/MnO₂) nanocomposite has been prepared via in situ electrochemical oxidation of mixture of aniline, *m*-aminobenzoic acid (MABA) and Mn²⁺ using fast cyclic voltammetry (CV). Tunnelling electron microscopy (TEM) clearly revealed the formation of nanofiber structure under the experimental conditions. Based on the electrochemical results, this nanocomposite shows high specific capacitance of 551 F g⁻¹ and high specific energy of 37.5 Wh kg⁻¹ at a current density of 5 mA cm⁻² in aqueous solution.

Keywords: Organic-inorganic nanocomposite; Self-doped polyaniline/MnO₂ nanocomposite; Supercapacitor.

Introduction

Nanostructured materials have opened a new opportunity for science and technology [1, 2]. Electroactive nanomaterials can improve the performance of electrochemical energy storage systems such as batteries [3] and supercapacitors [4]. Supercapacitors are considered as one of the newest innovations in the field of high power electrical energy storage systems. The main strategy has been employed to improve the energy characteristics of the supercapacitors is the use of nano-sized materials because of their unique physical and chemical properties. High surface area of such materials make the supercapacitors have higher specific capacitance than micro-sized materials based supercapacitors [5]. It is due to more participation of higher percentage of the electroactive materials and rapid ion diffusion which results in fast redox switching. The other benefit of using nano-structured materials is increasing the working voltage window [6]. Recently, many attempts of scientists have been focused on preparation of various types of organic-inorganic nanocomposite in the energy storage fields. It is due to their potential for combining properties that are difficult to attain separately with individual components [7].

In continuation our recent studies on the electrical energy storage systems based on SDPA [4, 8] and metal oxides [9, 10] for energy storage systems, in this work, we introduce a new organic-inorganic nanocomposite (SDPA/MnO₂) and evaluate their capability as active material in the supercapacitor.

Experimental

High purity grade of MABA, H₂SO₄ and Na₂SO₄ were purchased from Aldrich and used as received without further purification. Aniline (Merck) was used after purification by distillation under reduced pressure prior to use. All the solutions prepared by using doubly distilled water.

All electrochemical experiments were carried out by an Autolab General Purpose System PGSTAT 30 (Eco-chemie, Netherlands). A conventional three electrode cell was used in order to synthesis and study the SDPA/MnO₂ nanocomposite material as working electrode. A Pt wire and Ag/AgCl (KCl, saturated) were utilized as the counter and reference electrodes, respectively.

The SDPA/MnO₂ nanocomposite and SDPA nanofiber films were potentiodynamically electrodeposited between -0.2 to 1.4 V vs. Ag/AgCl at scan rate of 250 mV s⁻¹ for 100 cycles. Electrodeposition of the SDPA/MnO₂ nanocomposite was carried out onto the stainless steel in 0.1 M MnSO₄, 0.1 M aniline monomer, 0.1 M *m*-aminobenzoic acid and 0.5 M H₂SO₄ solutions. Moreover, the electropolymerization of the SDPA was performed on stainless steel in 0.1 M aniline monomer, 0.1 M *m*-aminobenzoic acid and 0.5 M H₂SO₄.

Results and Discussion

Morphological studies

Fig. 1 shows TEM of the formation of SDPA/MnO₂ nanocomposite. The SDPA and MnO₂ are randomly dispersed in the whole of nanofiberous structure of the nanocomposite. Due to the presence of MnO₂ in this structure, agglomeration of nanofibrous structure during charge-discharge process and swelling-shrinkage of SDPA is prevented.

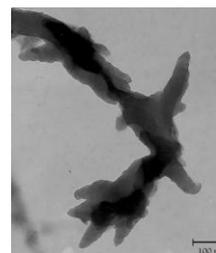


Fig. 1 TEM image of SDPA/MnO₂ nanocomposite.

Electrochemical studies

Fig. 2 shows the cyclic voltammograms of the SDPA/MnO₂ nanocomposite and the SDPA in a three electrode cell and potential ranges of -0.2 to 0.8 V vs. Ag/AgCl, at scan rate of 20 mV s⁻¹ in aqueous solution. As it is seen, the CV curves of the SDPA/MnO₂ and SDPA electrodes show two redox peaks could be attributed to reversibly charge/discharge processes of the SDPA component. However, SDPA/MnO₂ nanocomposite shows more electroactivity than the SDPA.

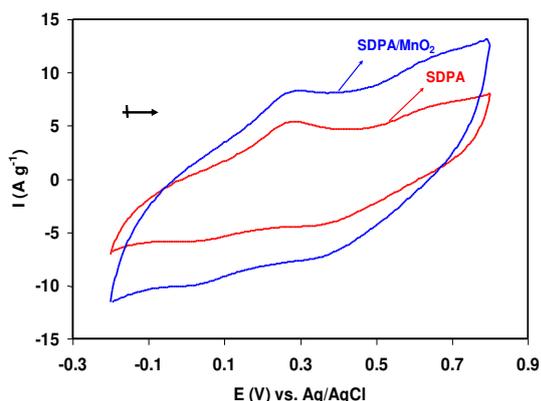


Fig. 2 Comparative CVs of the SDPA/MnO₂ nanocomposite and the SDPA in the three electrode cell at scan rate of 20 mV s⁻¹.

CV studies also were used to evaluate the capacitive behaviour of the system. The specific capacitances (C_{single}) of the SDPA/MnO₂ nanocomposite or the SDPA electrodes in the three electrode system ($F g^{-1}$) were calculated based on the following equation:

$$C_{single} (F g^{-1}) = \frac{I_{avg}}{sm} \quad (1)$$

where, I_{avg} is the average current (A) at cathodic branch of CV curve, s is the potential sweep rate ($V s^{-1}$) and m is amount of active materials in each of the supercapacitor electrode [11]. Based on the Eq. 1, the specific capacitance of the SDPA/MnO₂ nanocomposite was obtained 551 $F g^{-1}$.

Conclusions

Nanostructured of the SDPA/MnO₂ material was prepared by the cyclic voltammetry at scan rate of 250 mV s⁻¹. The application of this nanocomposite was evaluated as supercapacitor material. The nanocomposite has minimal degradation due to the presence of MnO₂. The specific capacitance of the SDPA/MnO₂ nanocomposite is 551 $F g^{-1}$.

Acknowledgment

The support of the Tarbiat Modares University Research Council is gratefully acknowledged.

References

- [1] D. I. Gittins, D. Bethell, D. J. Schiffrin, and R. J. Nichols, "A nanometre-scale electronic switch consisting of a metal cluster and redox-addressable groups," *Nature*, 408 (2000) 67-69.
- [2] R. Valiev, "Materials science: Nanomaterial advantage," *Nature*, 419 (2002) 887-889.
- [3] M. A. Kiani, M. F. Mousavi, and S. Ghasemi, "Size effect investigation on battery performance: Comparison between micro- and nano-particles of [beta]-Ni(OH)₂ as nickel battery cathode material," *Journal of Power Sources*, 195 (2010) 5794-5800.
- [4] H. R. Ghenaatian, M. F. Mousavi, S. H. Kazemi, and M. Shamsipur, "Electrochemical investigations of self-doped polyaniline nanofibers as a new electroactive material for high performance redox supercapacitor," *Synthetic Metals*, 159 (2009) 1717-1722.
- [5] C.-j. Liu, U. Burghaus, F. Besenbacher, and Z. L. Wang, "Preparation and Characterization of Nanomaterials for Sustainable Energy Production," *ACS Nano*, 4 (2010) 5517-5526.
- [6] D. Reyman, E. Guereca, and P. Herrasti, "Electrodeposition of polythiophene assisted by sonochemistry and incorporation of fluorophores in the polymeric matrix," *Ultrasonics Sonochemistry*, 14 (2007) 653-660.
- [7] Y. Fang, J. Liu, D. J. Yu, J. P. Wicksted, K. Kalkan, C. O. Topal, B. N. Flanders, J. Wu, and J. Li, "Self-supported supercapacitor membranes: Polypyrrole-coated carbon nanotube networks enabled by pulsed electrodeposition," *Journal of Power Sources*, 195 (2010) 674-679.
- [8] M. S. Rahmanifar, M. F. Mousavi, and M. Shamsipur, "Effect of self-doped polyaniline on performance of secondary Zn-polyaniline battery," *Journal of Power Sources*, 110 (2002) 229-232.
- [9] S. Ghasemi, M. F. Mousavi, H. Karami, M. Shamsipur, and S. H. Kazemi, "Energy storage capacity investigation of pulsed current formed nano-structured lead dioxide," *Electrochimica Acta*, 52 (2006) 1596-1602.
- [10] H. Karami, M. Shamsipur, S. Ghasemi, and M. F. Mousavi, "Lead-acid bipolar battery assembled with primary chemically formed positive pasted electrode," *Journal of Power Sources*, 164 (2007) 896-904.
- [11] W. Sun, R. Zheng, and X. Chen, "Symmetric redox supercapacitor based on micro-fabrication with three-dimensional polypyrrole electrodes," *Journal of Power Sources*, 195 (2010) 7120-7125.