Materials Chemistry and Physics 124 (2010) 29–32

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Materials science communication

Tetrapropylammonium-manganese oxide/polypyrrole hybrid nanocomposite thin films as novel electrode materials for supercapacitors

Suk Fun Chin*, Suh Cem Pang

Department of Chemistry, Faculty of Resource Science and Technology, Universiti Malaysia Sarawak (UNIMAS), 94300, Kota Samarahan, Sarawak, Malaysia

ARTICLE INFO

Article history:
Received 30 October 2009
Received in revised form 25 May 2010
Accepted 25 June 2010

Keywords:
Hybrid nanocomposites
Thin films
Heat treatment
Electrochemical properties

ABSTRACT

Tetrapropylammonium-manganese oxide/polypyrrole (TPA-MO/Ppy) hybrid nanocomposite with molar ratios of TPA-MO/Ppy 4:1, 2:1 and 1:1 were successfully prepared by a combination of *in situ* polymerization and the sol–gel process. The microstructure of hybrid nanocomposite thin film samples was observed to be significantly affected by synthesis parameters, most notably the molar ratio of reactants and post-synthesis calcination temperature. Samples with higher pyrrole contents appeared to possess higher specific surface areas, which ranged from 132 to 281 $m^2 g^{-1}$. SEM micrographs indicated that all nanocomposite thin films were highly fibrous and porous in nature. Optimum doping of manganese oxide with conducting polypyrrole had led to the formation of novel nanocomposite with nanofibrillar structures which consisted of interconnected manganese oxide and polypyrrole nanoclusters. Optimized nanocomposite films showed higher charge capacities which could be attributed to enhanced material utilization as a result of optimized microstuctural parameters in particular, specific surface areas.

1. Introduction

Manganese oxides in their various forms have been extensively studied and developed as electrode materials in supercapacitors [1–3]. Manganese oxide-based materials received particular attention and interest due to the low cost of raw materials, low toxicity and superior electrochemical performances. Our earlier studies have shown that tetrapropylammonium-manganese oxide (TPA-MO) thin films are promising electrode materials for the fabrication of thin film supercapacitors due to their high specific capacitance, good cycling reversibility and stability [1]. However, the major drawback of manganese oxide is its low electronic conductivity. Carbon powder such as acetylene black is generally being added to manganese oxides to improve their conductivities. However, such addition of materials without electrochemical activity tends to reduce the overall energy density of these electrode materials [4].

Recently, conducting polymers such as polypyrrole and polyaniline have been studied extensively as active electrode materials for supercapacitors due to their relatively high electronic conductivities and reversible redox reactions [5,6]. Although conducting polymers possess high conductivity, the brittleness, poor environmental stability and poor charge–discharge characteristics of these materials have hampered their widespread applications in such electrochemical devices. Several researchers have attempted to synthesize manganese dioxide/polypyrrole (MnO_2/Ppy) nanocomposite since the synergetic interaction of MnO_2 and Ppy would enhance the electrochemical performance and mechanical stability of the electrode. Sharma et al. have used electrochemical deposition method to prepare MnO_2/Ppy nanocomposite. In their studies, polypyrrole was being used as the support for the deposition of manganese oxide. A specific capacitance value as high as 600 $F g^{-1}$ was achieved for their MnO_2/Ppy thin film electrodes [7]. Carbon nanotube (CNT) supported MnO_2/Ppy has been synthesized by the chemical synthesis method in order to improve the dispersibility and surface area of MnO_2/Ppy [8,9]. However, much lower specific capacitance values of 268 and 281 $F g^{-1}$ were reported. The high specific capacitance observed in MnO_2 based electrode materials are mainly attributed to the pseudocapacitance arising from redox processes. The CNT in electrode materials did not contribute positively to the pseudocapacitance and hence resulted in decreased specific capacitance value for these CNT/MnO_2/Ppy electrode materials.

In this paper, we have reported on the synthesis of tetrapropylammonium-manganese oxide/polypyrrole (TPA-MO/Ppy) hybrid nanocomposite by a combination of *in situ* polymerization and sol–gel processes. In contrast to previous studies as reported in the literatures which produced spherical shaped MnO_2/Ppy nanocomposites [7–9], our synthesis approach has resulted in fibrous MnO_2/Ppy nanocomposite. Such fibrous structures had been demonstrated to be the more favorable morphology of electrode materials by providing short diffusion path-lengths for ions and excitons thereby giving rise to high charge–discharge rates. Furthermore, fibrous structures reduce the diffusion resistance of electrolytes during rapid charge–discharge

---

* Corresponding author. Tel.: +60 82 582999; fax: +60 82 583160.
E-mail address: sfchin@frst.unimas.my (S.F. Chin).

0254-0584/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.matchemphys.2010.06.060

processes [10–12]. Previous studies did not investigate the effects of heat treatment and chemical composition on the microstructure and morphology of the resulting MnO_2/Ppy nanocomposite. In this study, the physical and electrochemical properties of these fibrous MnO_2/Ppy nanocomposite thin films prepared under various synthesis parameters and post-synthesis heat treatment regimes were investigated. Our studies demonstrated that fibrous TPA-MO/Ppy nanocomposite under optimized synthesis conditions exhibited enhanced charge capacity, and a maximum specific capacitance of 870 F g^{-1} has been achieved.

2. Experimental

2.1. Chemicals

All chemicals used were of the analytical reagent grade from Aldrich and Fluka and used as received without further purification.

2.2. Sample preparation and characterization

Stable colloidal suspension of tetrapropylammonium-manganese oxide (TPA-MO) was prepared based on the synthesis procedures that had been described in our earlier paper [1]. Nanocomposites of tetrapropylammonium-manganese oxide/polypyrrole (TPA-MO/Ppy) were prepared by a combination of *in situ* polymerization of pyrrole and the sol–gel process. A known volume of pyrrole monomer was slowly added to a magnetically stirred TPA-MO colloidal suspension containing a fixed amount of $FeCl_3$ at room temperature. The observed gradual change in color from dark brown to black indicated the formation of polypyrrole. After stirred continuously for 4 h, the resulting suspension was centrifuged and the solid was washed with ultrapure water. The solid sample was then redispersed in ultrapure water by sonication, and followed by centrifugation. This process was repeated four times to ensure complete removal of $FeCl_3$. Finally, the solid sample was redispersed in ultrapure water by sonication to form TPA-MO/Ppy colloidal suspension. The manganese and pyrrole concentrations in the resulting colloidal suspension were determined quantitatively by the Atomic Absorption Spectroscopy (AAS) and the Total Organic Carbon analyzer (TOC) respectively.

TPA-MO/Ppy nanocomposite thin films were eletrodeposited (EPD) directly onto stainless steel plates by the electrophoretic deposition technique. A Field Emission Scanning Electron Microscope (FE-SEM, LEO Model 1525) was used to characterize the surface morphology of the electrodeposited TPA-MO/Ppy nanocomposite thin films. Xerogels were prepared by evaporating a known volume of TPA-MO/Ppy colloidal suspension under controlled conditions. The specific surface areas of xerogels were determined by the Brunauer–Emmett and Teller (BET) nitrogen gas adsorption–desorption method at 77 K using a BET Analyzer (Sorptomatic 1990). The electrochemical properties of the electrodeposited TPA-MO/Ppy thin films that have been heat treated at 300 °C in air for an hour were studied as the working electrode by cyclic voltammetry using a Potentiostat/Frequency Response Analyzer (PARSTAT 2263). For all electrochemical studies, a standard three-electrode cell configuration consisting of a saturated calomel electrode (SCE) fitted with a bridge of vycor frit as a reference electrode, a platinum foil ($\sim$6.25 cm^2) as the counter electrode, and 1.0 M Na_2SO_4 solution as the aqueous electrolyte. Cyclic voltammograms (CV) were obtained within the potential range of 0.0 and +0.9 V (versus SCE), with a scan rate of 50 mV s^{-1}. The charge capacity, Q was calculated from the CV curves according to Eq. (1):

$$Q(\mathrm{mC\,cm^{-2}}) = \int I\,dt = \int \frac{I}{dV/dt}\,dV \qquad (1)$$

where I is the instantaneous anodic current density (mA cm^{-2}) at a given potential and t is the sampling time in seconds.

3. Results and discussion

3.1. Specific surface areas

The effect of heat treatment on the specific surface areas of TPA-MO/Ppy nanocomposite xerogels was shown in Fig. 1. In general, specific surface areas were observed to increase gradually with calcination temperature up to 300 °C. This effect could be attributed to the removal of structural (physisorbed and chemisorbed) water content and the decomposition of organic solvent residues within the xerogel samples. However, the specific surface areas were observed to decrease for all xerogel samples that were calcined at 400 °C. At 400 °C, most of the structural water content and organic residues would have been eliminated in conjunction with the densification of samples. Xerogels prepared from the TPA-MO/Ppy (1:1) were observed to possess comparatively higher specific surface areas which ranged from 175 to 285 $m^2\,g^{-1}$ depending on the calcination temperatures. Xerogels derived from TPA-MO/Ppy (2:1) and TPA-MO/Ppy (4:1) possess relatively lower specific surface areas which ranged from 157 to 235 $m^2\,g^{-1}$ and 136 to 205 $m^2\,g^{-1}$, respectively.

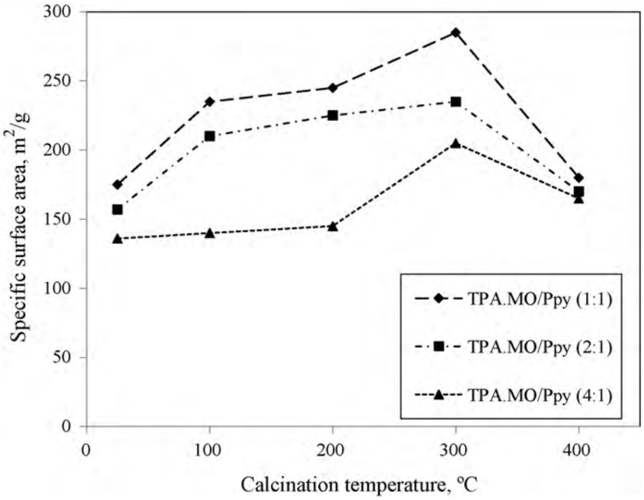

Fig. 1. Effect of calcination temperatures on the specific surface area of various TPA-MO/Ppy thin films.

3.2. Scanning electron microscopy (SEM)

Fig. 2 show SEM micrographs of TPA-MO and TPA-MO/Ppy nanocomposite thin films electrodeposited on the supporting stainless steel plates and heat treated at 300 °C in air for an hour. The morphology of the TPA-MO/Ppy nanocomposite thin films was observed to be distinctively different from that of TPA-MO thin films. TPA-MO thin films was observed to be densely packed and nanoparticulate in nature. The densely packed nanoparticles were not well resolved even under 300× magnifications (Fig. 2a). In contrast, the TPA-MO/Ppy nanocomposite thin films appeared to be highly porous and fibrous in nature with randomly dispersed nanoparticles being observed within the nanofibrillar structure of TPA-MO/Ppy (4:1) and TPA-MO/Ppy (2:1) nanocomposite films. As the polypyrrole content was increased, for instance from 25% in TPA-MO/Ppy (4:1) to 33% in TPA-MO/Ppy (2:1) such randomly dispersed nanoparticles were observed to have decreased substantially. The presence of these randomly dispersed nanoparticles could have resulted in the reduction of the specific surface area by closing or blocking pores within the xerogel samples. Besides, the diameter of nanofibers formed was observed to decrease with higher polypyrrole content in the nanocomposite. The fiber diameter was observed to vary from 30–50 nm in TPA-MO/Ppy (4:1) to 10–20 nm in TPA-MO/Ppy (1:1) xerogel samples. As observed in the SEM micrographs, TPA-MO/Ppy (1:1) nanocomposite thin films were highly fibrous and porous in nature, with no randomly dispersed nanoparticles being observed within these films.

Fig. 3 (a) and (b) shows the distinctively different morphological characteristics of manganese oxide/polypyrrole hybrid (1:1) nanocomposite thin films as prepared at 25 °C and after being calcined at 300 °C in air. Films without any heat treatment showed loosely packed, irregular and macroporous microstructure, whereas films that had been calcined at higher temperature was observed to be denser with very fine, uniform, and well defined nanofibrillar structure. The heat treatment at 300 °C could have burnt off a substantial portion of the organic components which