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

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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

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