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Self-assembled manganese dioxide nanowires as electrode materials for electrochemical capacitors

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ABSTRACT

The microstructure and morphology of sol–gel derived manganese dioxide (MnO_2) xerogels were affected by the synthesis conditions and post synthesis heat treatment. Manganese dioxide nanoparticles in sol that were dialyzed to more acidic pH (pH 5.7) value were observed to self-assemble into nanowires, whereas non-dialyzed sols remained nanoparticulate in nature. MnO_2 xerogels of disordered nanowire network exhibited comparatively higher porosity and BET surface areas. The electrochemical properties of both MnO_2 nanowire and nanoparticle thin-film electrodes were evaluated using cyclic voltammetry in a mild aqueous electrolyte (0.1 M Na_2SO_4). The charge capacities of MnO_2 nanowire-based thin-film electrodes were substantially higher (~800 F/g) than those of nanoparticulate thin-film electrodes (~700 F/g).

1. Introduction

Over the past decade, there has been a growing interest in the development of electrochemical capacitors (ECs) or supercapacitors as high power density charge storage devices due to the exponential growth of portable electronics and communication devices product such as laptops, cellular phones, MP3 players and personal digital assistants (PDA). Electrochemical capacitors are hybrid between batteries and conventional capacitors with higher energy density than conventional capacitors, and with longer cycle life as well as higher power density than batteries [1]. Many transition metal oxides have been shown to be excellent electrode materials for the fabrication of electrochemical capacitors. Hydrous ruthenium oxide ($RuO_2 \cdot xH_2O$) was shown to exhibit very high specific capacitance and good cycling reversibility [2,3]. A specific capacitance value as high as 720 F/g was reported for ruthenium oxide–carbon composite electrodes in strong acidic electrolytes [4]. However, these materials are very expensive, toxic in nature and require the use of strong acidic electrolytes (5 M H_2SO_4) which have limited their commercial applications. Thus, various metal oxides such as NiO_x, CoO_x, SnO_2 and MnO_x have been extensively investigated as alternative electrode materials for electrochemical capacitors [5–8]. Recently, several studies have shown that MnO_2 thin films are very promising electrode materials for the fabrication of electrochemical capacitors. These thin films have been shown to be chemically stable, high in specific capacitance and highly reversible [9,10]. A specific capacitance value as high as 700 F/g was achieved for MnO_2 thin films in mild aqueous electrolyte [11,12]. Furthermore, MnO_2 is low cost, non-toxic and environmentally friendly in nature.

The electrochemical property of the electrode materials is affected by their microstructure and morphology [13]. One-dimensional nanostructured materials such as nanotubes, nanowires and nanorods have demonstrated to be more favorable morphology for electrode materials as they provide short diffusion path-lengths to ions and excitons, leading to high charge/discharge rates [14]. Furthermore, one-dimensional nanostructure can reduce diffusion resistance of electrolytes in rapid charge/discharge processes. Nanowires of SnO_2 and V_2O_5 were shown to have significantly improved the rate capability of thin-film electrodes for electrochemical capacitors as compared to nanoparticulate thin-film electrodes [15–17].

Conventionally, MnO_2 nanowires were prepared by hydrothermal treatment of MnO_2 nanoparticles in water or ammonia solution at high temperature (120–160 °C) [18,19]. Recently, some researchers had used Pluronic P123 as structure directing agent to synthesize MnO_2 nanowires at room temperature [20]. However, this copolymer is very expensive and it is tedious to remove the copolymer from the end product after synthesis. In the present work, we have successfully prepared MnO_2 nanowires via the self-assembly of MnO_2 nanoparticles using the dialysis method. This synthesis approach is simple, without the need to use any structure directing surfactant or template, and can be carried out at ambient temperature. As such, this synthesis approach can potentially be used for commercial production of nanowire-based MnO_2 electrode materials suitable for the fabrication of thin-film electrochemical capacitors and other related charge storage devices. To the best of our knowledge, this is

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