

Research Article

The Capacitive Behaviors of Manganese Dioxide Thin-Film Electrochemical Capacitor Prototypes

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We have documented the fabrication of manganese dioxide (MnO_2) thin-film electrochemical capacitor (EC) prototypes with dual-planar electrode configuration. These EC prototypes exhibited good capacitive behaviors in mild Na_2SO_4 aqueous electrolyte. Enhanced capacitive behaviors of EC prototypes were observed upon prolonged voltammetric cycling which could be associated with microstructural transformation of MnO_2 thin-film electrodes from densely packed plate-like to irregular petal-like surface morphology. Effects of voltammetric scan rates, prolonged voltammetric cycling, electrolyte composition, and electrolyte concentration on the surface morphology of MnO_2 thin-film electrodes, and associated capacitive behaviors of MnO_2 thin-film EC prototypes were investigated by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge/discharge (GCD) techniques. Results of both CV and EIS indicated that thin-film MnO_2 EC prototypes exhibited the highest specific capacitance of 327 F/g in 0.2 M Na_2SO_4 aqueous electrolyte. Being environmentally benign and cheap, MnO_2 thin-film electrochemical capacitors have high potential utility as pulsed power sources, as well as load-leveling functions in various consumer electronic devices.

1. Introduction

The phenomenal increase in demands for electronic devices, power tools, and energy-intensive device applications necessitate the continual development of new generation energy-storage systems of high rate capability and performances. Energy-storage devices particularly pseudocapacitive electrochemical capacitors (ECs) fabricated using various nanoparticulate transition metal oxides have gained increasing interest among research scientists worldwide due to their high energy and power densities. Among them, manganese dioxide- (MnO_2 -) based electrodes have been reported to exhibit high specific capacitance which ranged from 130 to 700 F/g in mild aqueous electrolytes [1–3]. However, these capacitance values are still substantially lower than the theoretical value of 1,380 F/g which corresponds to the complete reduction of Mn^{4+} to Mn^{3+} . Low utilization of bulk MnO_2 electroactive material for electrical energy storage could be mainly attributed to microstructural factors associated with the electroactive material concerned. As

such, microstructural control at the nanoscale has been one of the major focuses in the development of novel electroactive materials that exhibit both high energy and power densities. Electroactive materials of desired pore size distribution, microstructure, composition, particles size, as well as electrochemically active functional groups could be precisely architected at nanoscale dimension [4]. However, the manufacturing of such electroactive materials required rigorous and expensive processing steps, and hence economically not feasible for commercial energy storage applications. To date, various types of electroactive materials such as nanostructured MnO_2 of nanofibers [5, 6], nanowires [7], sea urchin-like and clew-like shapes [8], carambola-like nanoflakes [9], and nanorods [10] have been synthesized by various approaches. However, none of these nanostructured MnO_2 materials could achieve the level of electrochemical performances close to the theoretical specific capacitance value of MnO_2 .

The microstructure and surface morphology of MnO_2 thin films are of particular interest since they influence the