Novel electrode materials for electrochemical capacitors: Part II. Material characterization of sol-gel-derived and electrodeposited manganese dioxide thin films

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Novel electrode materials for electrochemical capacitors: Part II. Material characterization of sol-gel-derived and electrodeposited manganese dioxide thin films

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Material characterization of sol-gel-derived and electrodeposited MnO_2 thin films showed that their microstructures are highly porous in nature. While sol-gel-derived films are nanoparticulate, electrodeposited films showed macropores of random and irregular platelike structures, comprising much denser surface layers and highly porous underlying layers. On the basis of calculated and theoretical density values of 1 and 4.99 g/cm^3, respectively, the porosity of sol-gel-derived MnO_2 films was determined to be as high as 80%, which is substantially higher than electrodeposited films at 67%. Apart from their higher specific capacitance, sol-gel-derived MnO_2 films appeared to exhibit higher cycling stability and reversibility than electrodeposited MnO_2 films. In the case of sol-gel films, thinner films appeared to exhibit higher cycling stability than thicker films. There was less alteration in surface morphology and microstructure, and the rate of loss in charge-storage capacity upon voltammetric cycling was not as significant for sol-gel MnO_2 thin films.

I. GENERAL INTRODUCTION

The proliferation in recent decades of modern and increasingly power-demanding portable electronics and communication devices necessitates the rapid development of charge-storage devices that are capable of meeting such an immense surge in portable power demand. Charge-storage devices, most notably batteries and electrochemical capacitors, which possess high power and energy density, high reversibility, and long cycle life are highly desirable for many of these applications. To ensure high portability and versatility of these systems, miniaturization of most device components is inevitable. At the same time, an increasing awareness and need for environmental protection and conservation, coupled with increasingly stringent environmental regulations, requires the continual development and utilization of cheap and environmentally benign materials for fabricating all charge-storage devices.

While the utility of manganese dioxide in batteries has long been recognized and well established, its potential application as an electrode material for electrochemical capacitors has not been extensively studied. Manganese dioxide (MnO_2) thin films are potentially novel electrode materials for electrochemical capacitors. These films are relatively conductive, are highly porous, and have high specific surface area. Furthermore, as an inorganic oxide composed of multivalent ions, manganese dioxide possesses such important characteristics as inherent nonstoichiometric character and a low bandgap for fast surface adsorption and desorption reactions. Electrode materials having these characteristics are expected to exhibit high pseudocapacitance associated with both surface and bulk redox processes. In addition, with an appropriate choice of electrolyte and under suitable operating conditions, manganese dioxide is chemically stable. Last, MnO_2 thin films can be easily prepared, are inexpensive, and are environmentally friendly.

The electrochemical properties of both sol-gel-derived and electrodeposited MnO_2 thin films have been reported in our earlier papers.[1,2] Sol-gel-derived MnO_2 films have been shown to possess higher charge storage capacity, specific capacitance, and exhibit higher cycling stability and reversibility in an unbuffered neutral electrolyte than those of electrodeposited films. Apart from a sizable contribution from double-layer capacitance, the capacitance of MnO_2 thin films is believed to be predominantly due to pseudocapacitance as a result of redox processes associated with the homogenous reduction of MnO_2 to MnOOH. This involves the incorporation of protons and electrons into the MnO_2 lattice through a double injection process.[3–7] Many studies have shown that large specific capacitances of electrochemical capacitors can be achieved through one or a combination of these charge storage mechanisms.[8–13]

In this paper, we have reported the material characterization of both sol-gel-derived and electrodeposited MnO_2 thin films using various established characteriza-

