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Research Article

Preparation and Characterization of Self-Assembled Manganese Dioxide Thin Films

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Thin films of manganese dioxide (MnO_2) were prepared by self-assembly of MnO_2 nanoparticles directly unto nickel-coated poly(ethylene terephthalate) flexible films using the newly developed horizontal submersion process. The thickness of deposited thin films was controllable by the deposition duration. This horizontal submersion deposition process for thin-film deposition is relatively easy, simple, and cost effective. Effects of deposition duration and calcination temperatures on the microstructure and electrochemical properties of self-assembled MnO_2 thin films were investigated. Optimized MnO_2 thin films exhibited high charge capacity, good cycling reversibility, and stability in a mild aqueous electrolyte and are thus promising electrode materials for the fabrication of thin-film electrochemical capacitors.

1. Introduction

Manganese dioxide- (MnO_2-) based thin film electrochemical capacitors have received numerous attentions since Pang et al. reported a specific capacitance value of 720 F/g for ultra-thin MnO_2 films in a mild aqueous electrolyte [1, 2]. MnO_2 thin films appear to be a promising electrode material in batteries and electrochemical capacitors due to the low cost of raw materials, low toxicity and environmentally benign, and their excellent electrochemical properties [3, 4]. Many routes for the preparation of MnO_2 thin films have currently been developed, which include the sol-gel process, electrodeposition [5–7], and atomic layer deposition [8]. More recently, the self-assembly technique has emerged as one of the most promising methods for thin film fabrication [9]. Self-assembly is the spontaneous adsorption process by which molecules or nanoparticles are arranged into organized aggregates, networks, or patterns onto a supporting substrate. It is characterized as being relatively simple, inexpensive, and requires low energy consumption.

In this study, we have attempted to prepare self-assembled manganese dioxide (MnO_2) thin films directly on nickel-coated poly(ethylene terephthalate) (Ni/PET) flexible supporting substrate using the newly developed horizontal submersion process under ambient conditions. This thin film deposition process is very cost effective, rapid, and conformal in the preparation of nanostructured thin films which are suitable for the fabrication of thin film electrochemical capacitors. Most notably, the thickness of deposited film is controllable simply by the duration of submersion or by repeating the deposition process a desired number of times. Physical and electrochemical characterization of manganese dioxide nanoparticles and self-assembled thin films was conducted using various established characterization techniques. The effect of deposition conditions on the microstructure and electrochemical properties of self-assembled manganese dioxide thin films were investigated.

2. Materials and Methods

2.1. Preparation of MnO_2 Colloidal Suspension (sol). Stable MnO_2 colloidal suspension (sol) was prepared based on a method reported in literature [10]. Typically, MnO_2 sol was prepared by mixing 4 mL of $KMnO_4$ (1.0×10^{-1} mol/L) and 8 mL of $Na_2S_2O_3$ (1.88×10^{-2} mol/L) in 38 mL ultrapure water (18.2 MΩ). The resulting dark-brown MnO_2 sol was