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Effects of thickness and electrolytes on the capacitive characteristics of anodically deposited hydrous manganese oxide coatings

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Abstract

An amorphous nanostructured hydrous manganese oxide ($MnO_2 \cdot nH_2O$) coating was anodically deposited onto a graphite substrate from an aqueous $MnSO_4$ solution. Various deposition charges were employed to achieve different coating thickness. The capacitive characteristics of the as-grown MnO_2 coatings were evaluated in various neutral alkali metal chloride solutions by cyclic voltammetry and chronopotentiometry. The as-grown MnO_2 coatings exhibited a capacitance of 275 F g^{-1} in a 0.5 M KCl solution. Dependence of coating thickness and electrolytes on the capacitive properties of MnO_2 coatings was demonstrated. The relationship of C_a with the deposition charge exhibits linearity in the range of 4.0 C cm^{-2}, and there is a peak at around 4.5 C cm^{-2}, however, the value of C_m keeps diminished. With the increase of the discharge current density, more rapid decrease of the specific capacitance was found when measured in the electrolyte with larger hydrated alkali metal cation in the order of $Li^+ > Na^+ > K^+$. This was especially noted for thicker MnO_2 coatings.

Keywords: Electrochemical capacitance; Anodic deposition; MnO_2 coatings; Thickness; Electrolytes

1. Introduction

Pseudo-capacitance, as a key form of electrochemical capacitance, is based on a faradaic charge exchange process involving an intercalation of ions and electrons into the electrode material itself. Significantly, ruthenium oxide exhibits a specific capacitance as high as 750 F g^{-1} [1,2], and thus has initially been employed for these electrochemical capacitors in military applications. The lack of abundance and high cost of the precious ruthenium are however the major disadvantages for commercial applications. More effort has thereby been directed to alternative inexpensive electro-active materials for electrochemical capacitor applications, such as nickel oxide [3–8], cobalt oxide [9–11], manganese oxide [12–15], vanadium oxide [16,17], and magnetite [18].

In view of both the inexpensiveness and the less toxicity, manganese oxide has recently been in the spotlight among the above mentioned as a capacitive material. It is however worth pointing out that pure $MnO_2 \cdot nH_2O$ via chemical co-precipitation exhibits poor capacitive characteristics mainly owing to the high resistance of the bulk [19]. Accordingly, MnO_2 films have been extensively studied for electrochemical capacitance. Pang et al. [12,13] reported a specific capacitance of 700 F g^{-1} with very thin MnO_2 films derived from sol–gel routes. Electrochemical-deposition techniques have advantages to control the morphology, microstructures, and properties of the deposits over the chemical syntheses. Hu and Tsou [20,21] have shown

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that anodically electrodeposited amorphous a-$MnO_2 \cdot nH_2O$ in thicker layers achieves specific capacitance more than 265 F g^{-1}. In addition, various electrochemical techniques, such as potentiostatic [22], galvanostatic [23], potentiodynamic [24], and cyclic voltammetric electrodeposition [25] were employed to grow nanostructured hydrous manganese oxide for improved capacitive performance. As reported in the literature [24], the use of high scan rate for the potentiodynamic deposition leads to the formation of amorphous nanostructured hydrous manganese oxide with micropores. Consequently, the electrolyte could seep into the micropores of nanostructured deposit. The formation approach plays an important role for the increase in specific capacitance with an increase in the thickness of the films. Effects of electrochemical-deposition mode and microstructures on the capacitive characteristics of nanostructured hydrous manganese oxide were also demonstrated by Miura et al. [26]. More significantly, Brett et al. [27] investigated some variations in MnO_2 anodic electrodeposition for electrochemical capacitors, and observed a consistent decrease in specific capacitance (from 260 to 50 F g^{-1}) as the deposit thickness increases.

In the present work, hydrous a-$MnO_2 \cdot nH_2O$ was anodically deposited onto a graphite substrate from an aqueous manganese sulfate solution, and characterized as an electrochemical capacitor electrode in different neutral aqueous electrolytes of alkaline metal salts. The aim of this study is to clarify possible impact of thickness and electrolyte type on the capacitive characteristics of the as-grown a-$MnO_2 \cdot nH_2O$ coatings.

2. Experimental

A graphite disc electrode (6 mm in diameter) was prepared in a procedure described in detail elsewhere [15]. The electrochemical cell for deposition was a three-electrode cell, in which a graphite disc was used as the working electrode, and a platinum gauge as the counter electrode, and an Ag/AgCl (3 M KCl) electrode as the reference, respectively. Before deposition, pH value of the deposition solution, consisting of 0.25 M $MnSO_4$, was adjusted to around 6.5 with a solution of 0.1 M H_2SO_4. It was observed that galvanostatic depositions could become unstable at higher currents with significant potential swings producing uncontrollable experimental conditions. A current density of 2.5 mA cm^{-2} was thus deliberately applied for specified time to achieve desired deposition charge on a CHI760B computer-controlled electrochemical workstation. The as-grown coatings were rinsed with, and cleaned ultrasonically for 10 min in distilled water, and then dried by a flow of cool air.

The surface morphology of the coatings was inspected on a JEOL JSM-5800LV scanning electron microscope (SEM). The thickness of the coatings was evaluated via SEM cross-sectional observations. In order to prepare a sample for an observation, a part of the electrode with

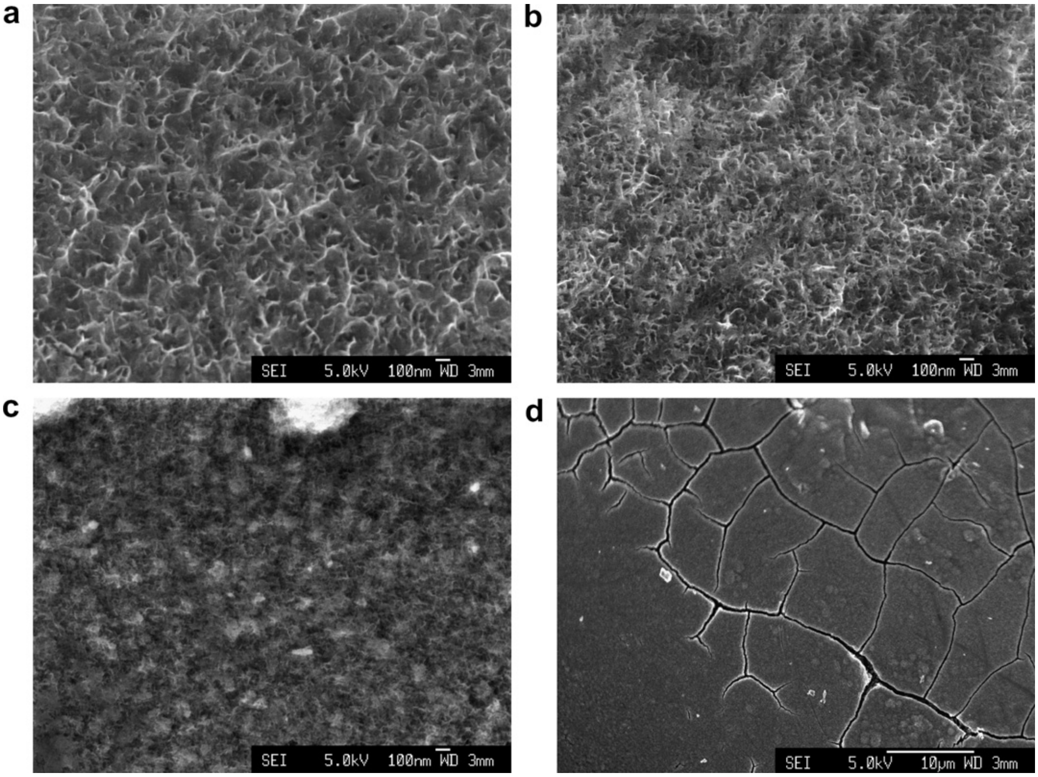

Fig. 1. SEM images of the surface of MnO_2 coatings grown at 0.4 C cm^{-2} (a), 2.0 C cm^{-2} (b), and 4.0 C cm^{-2} (c), respectively. (d) is at a lower magnification of (c).