

Production of capacitive films from Mn thin films: Effects of current density and film thickness

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Received 2 May 2005; accepted 2 June 2005

Available online 18 August 2005

Abstract

Electrochemical oxidation of Mn thin films produces a highly capacitive, porous MnO₂ surface layer. The effects of current density and deposited Mn layer thickness on the morphology of the porous surface layer are quite pronounced. A higher current density results in a much thinner, finer porous layer while thicker deposited Mn films give much thicker porous films. Increasing the current density results in a film with greater hydration and an increase in capacitance. For the films of varying deposited layer thickness, oxidation occurs at a single current density and, as a result, the relative hydration of the film does not change noticeably. Increasing the deposited layer thickness results in a porous surface layer that increases in thickness, but with a constant amount of hydration. This combination of trends results in a significant increase in the areal capacitance of the film but little change in the specific capacitance.

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Keywords: Scanning electron microscopy; Manganese oxide; Electrochemical supercapacitor; Physical vapor deposition; X-ray photoelectron spectroscopy

1. Introduction

Electrochemical pseudocapacitors are used primarily for applications that require a high power output and a high cycle capacity [1,2]. Traditionally, ruthenium oxide has been the material primarily used for these pseudocapacitors and exhibits specific capacitance values of up to 750 F g⁻¹. However, raw material costs and toxicity have made ruthenium difficult to produce as a commercial product [2].

Manganese oxides may provide a lower cost and lower toxicity replacement for ruthenium oxides in capacitor applications [3]. In the past, MnO₂ films have been created through chemical reaction or electrochemical deposition resulting in an amorphous hydrated MnO₂ product or a nanocrystalline hydrated MnO₂ product [3–8]. Brett et al. have used physical

vapor deposition of a manganese layer followed by electrochemical oxidation in a Na₂SO₄ solution to produce a surface film that can develop up to 700 F g⁻¹ in capacitance [9–11,14]. The Mn layer produced by PVD is a two-phase mixture of Mn and MnO [10]. The electrochemical oxidation step produces a highly porous, hydrated, amorphous MnO₂ film [11]. This porous film is the key to developing the high capacitance recorded by these films. Small changes in film morphology and chemistry can significantly affect the resulting capacitance. Preliminary studies about the effects of deposited film thickness on the resulting capacitance [14] have shown an increase in planar capacitance with increasing film thickness; however, there is little corresponding analysis of the films to aid in the explanation of the results. The purpose of this paper is to explore the effects of oxidation current on the resulting porous layer and the effects of the starting film thickness on the porous layer. Ultimately, the effects of the morphology and chemistry of the porous film will be related to the capacitance.

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2. Experimental procedure

Thin manganese films were fabricated in a sputter deposition system using a 50 mm 99.95% Mn target and a target to substrate distance of 457 mm. The base pressure was 3×10^{-7} Torr and the pressure in the chamber during deposition was 6–7 mTorr. The sputtering gas was argon fed in at a rate of 10 sccm. Sputtering was carried out under constant power operation at 200 W. The manganese was deposited onto a Si substrate coated with a standard Ti/Pt metallization layer (25 nm Ti and 300 nm Pt). Samples with a nominal 50 nm Mn layer thickness were used to study the effect of oxidation current on the capacitance. To study the effect of the PVD manganese layer thickness on the capacitance of the films, samples with Mn layer thicknesses of 25, 60, 110 and 230 nm were used.

Electrochemical oxidation occurred in 1 M Na₂SO₄ electrolyte using a Gamry 750 potentiostat, with an Ag/AgCl reference electrode and a Pt wire as the counter electrode. Samples were electrochemically oxidized by applying a constant anodic current over a specified time period (galvanostatically) until the potential of the film reached 0.9 V (beyond 0.9 V, the film delaminates). A current density of 0.1 mA cm⁻² was used to oxidize the samples of variable thickness (25, 60, 110 and 230 nm). Current densities of 0.2, 0.4, 0.8 and 1 mA cm⁻² were used to evaluate their effect on capacitance. Capacitance was measured using cyclic voltammetry (CV) cycling at a rate of 50 mV s⁻¹ between 0 and 0.9 V. The capacitance was estimated from the current versus time curve. Integrating the area underneath the current versus time curve between 0 and 0.9 V provided an estimate of the total charge capacity of the film. An estimate of the capacitance of the film was then determined by dividing the charge capacity by the change in voltage (0.9 V).

The samples were imaged in a JEOL field emission scanning electron microscope (FE-SEM) at 5 kV without conductive coating. Surface analysis of the films was done by X-ray photoelectron spectroscopy (XPS) using a Kratos AXIS 165 X-ray Photoelectron Spectrometer. A monochromatic Al source was used operating at 210 W with a pass energy of 20 eV and a step of 0.1 eV. The XPS analysis was carried out using a procedure developed by Chigane and Ishikawa [12,13]. The valence of the Mn in the film was determined from the Mn 3s peak splitting widths (Table 1) and the hydration was determined from the de-convolution of the O 1s spectra (Table 2) into the Mn–O–Mn, Mn–O–H and H–O–H components.

Table 1
Mn 3s peak splitting values for various manganese oxides

Sample	Mn 3s splitting width, ΔE (eV)	Valence of Mn
MnO	5.79–5.8	2
Mn ₃ O ₄	5.3–5.50	2, 3
Mn ₂ O ₃	5.2–5.41	3
MnO ₂	4.7–4.78	4

Table 2
O 1s deconvolution energies for different bonds

Bond type	Binding energy (eV)
Mn–O–Mn	529.3–530.0
Mn–O–H	530.5–531.5
H–O–H	531.8–532.8

3. Results/discussion

3.1. Effects of oxidizing current density

PVD deposited manganese films were electrochemically oxidized to a final potential of 0.9 V using varying current densities. The total oxidation time follows an exponential decay trend (Fig. 1). The downward trend is reasonable since higher current densities result in faster oxidation rates and therefore less time required to reach 0.9 V versus Ag/AgCl. The effect of current density on the morphology of the porous layer is quite pronounced. The higher current densities produce a porous layer that is very fine and much thinner (Fig. 2), resulting in an overall reduction in the exposed surface area.

The XPS analysis (Table 3) gives both the valence of the manganese in the porous film and the relative hydration of these films. Using the highest current density results in incomplete oxidation and a two-phase mix of MnO₂ with trace amounts of Mn₂O₃. The most likely explanation for this is that the imposed oxidation rate is too rapid at the higher current density to completely oxidize the porous layer prior to reaching 0.9 V. There is an overall increase in the hydration of the film with increasing oxidizing current density. The result is two competing effects. Film hydration increases with increasing current density, which should have a positive effect on capacitance. Only the hydrated lattice sites are believed to take part in the capacitive process and therefore increased hydration in the structure means more sites are available to contribute to the overall capacitance of the film [1]. There is a simultaneous reduction in the thickness of the porous film and the exposed surface area as well, which will reduce capacitance (Fig. 2).

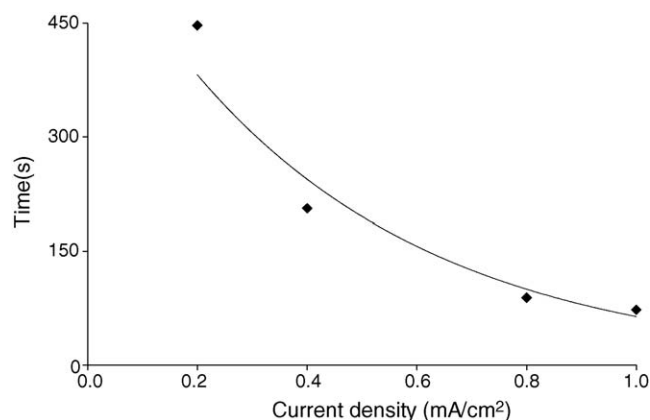


Fig. 1. Oxidation time as a function of current density for 50 nm thick Mn films.

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