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Microstructure and properties of manganese dioxide films prepared by electrodeposition

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ABSTRACT

Nanostructured manganese dioxide films were obtained by galvanostatic, pulse and reverse pulse electrodeposition from 0.01 to 0.1 M $KMnO_4$ solutions. The deposition yield was investigated by in situ monitoring the deposit mass using a quartz crystal microbalance (QCM). Obtained films were studied by electron microscopy, X-ray diffraction analysis, energy dispersive spectroscopy, thermogravimetric and differential thermal analysis. The QCM and electron microscopy data were utilized for the investigation of deposition kinetics and film formation mechanism. It was shown that the deposition rate and film microstructure could be changed by variation of deposition conditions. The method allowed the fabrication of dense or porous films. The thickness of dense films was limited to ~0.1 μm due to the insulating properties of manganese dioxide and film cracking, attributed to drying shrinkage. Porous and crack-free 1–2 μm films were obtained using galvanostatic or reverse pulse deposition from 0.02 M $KMnO_4$ solutions. It was shown that film porosity is beneficial for the charge transfer during deposition and crack prevention in thick films. Moreover, porous nanostructured films showed good capacitive behavior for applications in electrochemical supercapacitors. The porous nanostructured films prepared in the reverse pulse regime showed higher specific capacitance (SC) compared to the SC of the galvanostatic films. The highest SC of 279 F/g in a voltage window of 1 V was obtained in 0.1 M Na_2SO_4 solutions at a scan rate of 2 mV/s.

1. Introduction

Electrodeposition of oxides is an important technique for the surface modification of materials and fabrication of nanostructured films for electronic, catalytic, biomedical and electrochemical applications [1–7]. Oxide films can be obtained using anodic oxidation or cathodic reduction methods [1,2,8]. Electrochemical methods are especially attractive for the fabrication of manganese dioxide films. The analysis of literature indicates that manganese dioxides with various crystalline structures are important materials for lithium batteries [9], alkaline Zn/MnO_2 cells [10], catalysts [11], sensors [12] and electrochemical supercapacitors [13]. The properties of MnO_2 are influenced by crystalline structure, particle size, shape and surface area. Many applications of MnO_2 are based on the use of porous nanostructured films. The microstructure of manganese dioxide films is especially important for the development of electrochemical supercapacitors and batteries, where small particle size, high surface area and porosity enable electrolyte access to the active material. A complicating factor in the fabrication of MnO_2 films by chemical methods is the lack of stable Mn (IV) precursors in aqueous solutions. However, manganese dioxide films can be prepared by electrochemical methods, using anodic oxidation of Mn^{2+} or cathodic reduction of Mn^{7+} species. The use of cationic Mn^{2+} species for anodic electrodeposition or anionic MnO_4^- (Mn^{7+}) species for cathodic electrodeposition requires the understanding of the deposition mechanisms and kinetics of deposition, which are influenced by diffusion, electromigration, kinetics of electrochemical reactions and other factors. Many investigations have been focused on the anodic electrodeposition of manganese dioxide films [14–17]. This method leads to the formation of γ-MnO_2 (also called electrolytic manganese dioxide [18]). Extensive studies have shown that microstructure and properties of manganese dioxide films can be varied by the variation of bath composition and by the use of additives. Different techniques were used for the anodic deposition, including galvanostatic, potentiostatic, potentiodynamic and pulse deposition [14–17,19,20]. Electrochemical quartz crystal microbalance (QCM) has been used for the investigation of deposition kinetics and deposition mechanism [21].

The interest in the development of cathodic electrodeposition stems from the possibility of co-deposition of other materials and chemical modification of manganese dioxide films for the

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fabrication of composite films with improved properties. It is in this regard that various metals, oxides and hydroxide materials can be deposited cathodically and the problem of anodic oxidation of the metallic substrates can be avoided.

The goal of this investigation was the fabrication of manganese dioxide films from $KMnO_4$ solutions by cathodic electrodeposition. In the galvanostatic and pulse deposition experiments described below, the deposition yield was studied in situ using quartz crystal microbalance. We report the influence of deposition conditions and $KMnO_4$ concentration on microstructure and properties of the films for applications in electrochemical supercapacitors.

2. Experimental procedures

Electrodeposition was performed from the 0.01–0.1 M $KMnO_4$ (Aldrich) aqueous solutions. The electrochemical cell for deposition included a substrate and a platinum counter electrode. The deposits were obtained on stainless steel foils (50 mm × 50 mm × 0.1 mm) and gold-coated quartz crystals, used as substrates. The deposition process has been monitored using a quartz crystal microbalance (QCM 922, Princeton Applied Research) controlled by a computer. The deposit mass Δm was calculated using Sauerbrey's equation [22]:

$$-\Delta F = \frac{2F_0^2}{A\sqrt{\rho_q \mu_q}}\Delta m \qquad (1)$$

where ΔF is frequency decrease of the QCM, F_0 is the parent frequency of QCM (9 MHz), A is the area of gold electrode (0.2 cm^2), ρ_q is the density of the quartz (2.65 g cm^{-3}) and μ_q is the shear modulus of quartz (2.95×10^{11} dyne cm^{-2}).

The deposits were scraped from the stainless steel substrates for X-ray diffraction (XRD) study, thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The phase content of the deposits was determined by XRD with a diffractometer (Nicolet I2) using monochromatic Cu Kα radiation at a scanning speed of 0.5 °/min. TGA and DTA studies were carried out in air between room temperature and 1000 °C at a heating rate of 5 °C/min using a thermoanalyzer (Netzsch STA-409). The microstructure of the coatings deposited on stainless steel substrates was investigated using a JEOL JSM-7000F scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS).

Capacitive behavior of the deposited films was studied using a potentiostat (PARSTAT 2273, Princeton Applied Research) controlled by a PowerSuite electrochemical software. The surface area of the stainless steel working electrodes was 1 cm^2. A three-electrode cell contained a working electrode, a platinum gauze counter electrode and a standard calomel reference electrode (SCE). Testing was performed in the 0.1 M Na_2SO_4 aqueous solutions, degassed with purified nitrogen gas.

Cyclic voltammetry (CV) studies were performed within a potential range of 0–1.0 V versus SCE at scan rates of 2–100 mV/s. The SC was calculated using half the integrated area of the CV curve to obtain the charge (Q), and subsequently dividing the charge by the mass of the film (m) and the width of the potential window (ΔV):

$$C = \frac{Q}{m\,\Delta V} \qquad (2)$$

3. Results and discussion

Cathodic deposits were obtained using galvanostatic and pulse deposition. Fig. 1 shows that deposit mass increased with increasing deposition time at a constant current density. Higher deposition yield was obtained at a higher current density (Fig. 1). These results indicate that the amount of the deposited material and film thickness can be varied. The deposition mechanism can be attributed to the diffusion and cathodic reduction of anionic MnO_4^- species. The reduction of MnO_4^- species and precipitation of manganese dioxide are in agreement with the Pourbaix diagram for Mn [23]. However, only limited information is available in the literature related to the complex chemistry of the reduction of MnO_4^-. The kinetic pathway of reducing Mn^{7+} to Mn^{4+} depends on electrode potential, pH, concentration of MnO_4^- and other species in the solutions. In neutral aqueous solutions the following reaction [23] can result in the reduction of MnO_4^- species:

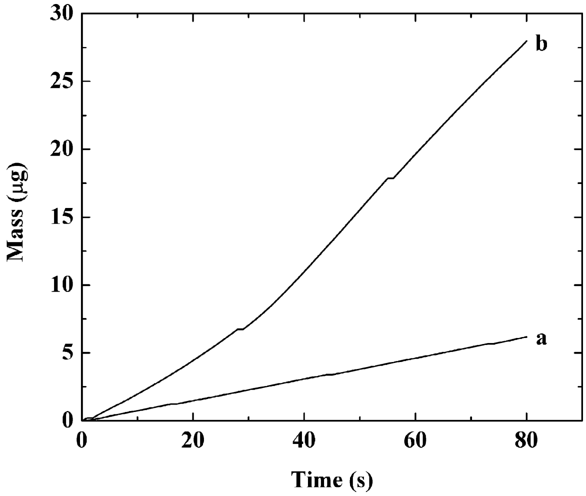

Fig. 1. Deposit mass versus deposition time for deposits obtained from the 0.02 M $KMnO_4$ solutions at current densities of (a) 1 mA/cm^2 and (b) 3 mA/cm^2.

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^- \qquad (3)$$

The results presented in Fig. 2 indicate that the deposition rate decreased with increasing $KMnO_4$ concentration. It is suggested that the deposition rate is governed by diffusion–electromigration kinetics in the $KMnO_4$ solutions. When a negatively charged MnO_4^- ion is reduced cathodically, it has to approach the cathode by diffusion against an adverse potential gradient. In concentrated solutions, the interactions between ions can result in enhanced friction effect. It is important to note, that the decrease in diffusion

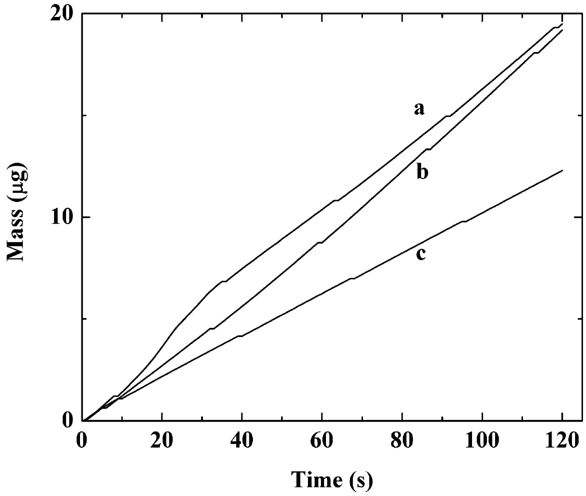

Fig. 2. Deposit mass versus deposition time for deposits prepared from (a) 0.01 M, (b) 0.02 M and (c) 0.1 M $KMnO_4$ solutions at a current density of 2 mA/cm^2.