

Hydrous–ruthenium–oxide thin film electrodes prepared by cathodic electrodeposition for supercapacitors

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Abstract

Hydrous ruthenium oxide ($\text{RuO}_2 \cdot n\text{H}_2\text{O}$) thin film electrodes were fabricated by cathodic electrodeposition on titanium substrates. The surface morphological characteristics of the $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ films were examined by scanning electron microscopy, and their images show the uniform spherical grains with nanometer sizes and porous network structure of the $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ films on Ti substrate. The electrochemical performances of the composite for supercapacitors were investigated by cyclic voltammetry, electrochemical impedance spectroscopy and charge/discharge technique. The $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ films exhibit good capacitive behavior, such as high reversible characteristics, excellent cycle stability, and superior power characteristics. The maximum specific capacitance of the $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ film electrode is 786 F g^{-1} achieved with deposit mass of 0.17 mg. © 2008 Elsevier B.V. All rights reserved.

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1. Introduction

The desired electrical properties for an efficient supercapacitor are long recycle life, high power output, high storage capacity and characteristic profile for quick charge/discharge [1]. These devices over the last few years have received considerable attention, due to their potential applicability in energy storage devices [2]. Supercapacitors store energy mainly by means of non Faradic charge separation across the electrical double-layer [2] and fast Faradic redox reactions within the electrode materials [3]. The materials for electrical double layer capacitors include aerogel carbons [4] and activated carbon [5] with high specific surface area, for the capacitance predominantly depends on the surface area accessible to the electrolyte ions [6]. On the other hand, Faradic processes to store energy need electro-active materials with high reversibility for fast charge transfer reactions between the electrode and the species present in the electrolyte. Transition metal oxides with considerable surface area [7,8] and conducting polymers [9]

are considered to be potential electrode materials for supercapacitors. Noble metal oxides have been identified as ideal electrode materials for supercapacitors due to their great specific capacitance, wide potential windows, and high electrochemical stability. Hence, the materials associated with fast Faradic redox processes on high surface area are recognized as the most promising candidates for supercapacitors.

Ruthenium oxide (RuO_2) is well-known electrode material with high electrochemical reversibility and a high specific capacitance for supercapacitors. The amorphous RuO_2 prepared by a sol–gel method exhibit a high specific capacitance of 720 F g^{-1} , which results from the surface Faradic redox reactions between Ru ions and H ions in the H_2SO_4 electrolyte [10]. RuO_2 has great merits in terms of high specific capacitance, highly reversible redox reactions in wide potential windows and a low electrochemical series resistance (ESR). However, it is more expensive than carbon based materials, which can be offset with construction with carbon–ruthenium composites in the form of hydrated thin films [11–13].

A thin film of hydrous ruthenium oxide ($\text{RuO}_2 \cdot n\text{H}_2\text{O}$) was electrodeposited onto a titanium (Ti) substrate by cyclic voltammetry (CV). The precision and the properties of the film,

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were affected by growth generations, applied potential and sweep rate [14,15]. In our present work, the $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ films were fabricated by a cathodic electrodeposition method with current density of 25 mA cm^{-2} , and their electrochemical properties were investigated via CV and charge/discharge technique.

2. Experimental details

$\text{RuO}_2 \cdot n\text{H}_2\text{O}$ deposits were directly electrodeposited on commercial 99.99% titanium substrates ($10 \text{ mm} \times 10 \text{ mm} \times 2 \text{ mm}$) from an aqueous, acidic solution of ruthenium chloride solution. Prior to electrodeposition, these Ti substrates were mechanically polished first using silicon carbide grit 600 power and then diamond compound paste (Klingspor, Germany). The substrates were immersed in an acetone ultrasonic bath for 30 min to remove any remainder particles and degreased with soap and water. Then the Ti substrates were etched in an oxalic acid ($\text{HO}_2\text{CCO}_2\text{H}$) solution at $90 \text{ }^\circ\text{C}$ for 1.5 h to remove the oxide layers. The etched substrates were completely rinsed using ultrapure water again, and then placed in plating solution. The exposed surface area of Ti substrates is equal to 1 cm^2 . The films studied here were deposited at room temperature in a plating bath consisting of $5 \text{ mM RuCl}_3 \cdot 3\text{H}_2\text{O}$ (Johnson Matthey, U.K.), 0.01 M HCl , and 0.1 M KCl , with the initial pH value kept at 2.0. The growth of $\text{RuO}_x \cdot n\text{H}_2\text{O}$ films was carried out by means of a cathodic deposition method. The pretreated Ti substrate was placed as the cathode electrode, a platinum (Pt) sheet ($2 \times 2 \text{ cm}^2$) was used as the counter electrode, and deposition was carried out in these solutions at applied current of 25 mA cm^{-2} for 8 min. After deposition, $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ films were dried in a furnace at $150 \text{ }^\circ\text{C}$ for 2 h.

Microstructural study of the $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ film was examined by a scanning electron microscope (SEM, HITACHI S-4700). All solutions used in this work were prepared with $18 \text{ M}\Omega \text{ cm}$ water produced by reagent water system (MILLI-Q SP, Japan). The weight of the deposits was measured using a balance (AB135-S, Mettler Toledo, Germany). Deposition of $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ was carried out by a potentiostat/galvanostatic (EG&G-PAR mode 273) meanwhile CV, galvanostatic charge/discharge, and electrochemical impedance spectroscopy (EIS) measurements of the $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ film electrode were performed by Potentiostat/Galvanostat IM6ex (ZHANER Elektrik; Germany). All experiments were carried out with a conventional three-electrode system with the $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ film electrode as the working electrode, saturated calomel electrode (SCE) as a reference and a Pt plate ($2 \times 2 \text{ cm}^2$) as counter electrode. The $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ film electrode was characterized electrochemically in $0.5 \text{ M H}_2\text{SO}_4$ solution at room temperature.

3. Results and discussion

3.1. Textural characteristic of $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ deposits

The typical surface morphologies of the deposit with different magnifications are respectively shown as photographs (a), (b), and (c) in Fig. 1 (Fig. 1(b) is magnified ten times of Fig. 1(a), Fig. 1(c) is magnified 100 times of Fig. 1(a)). Noted that

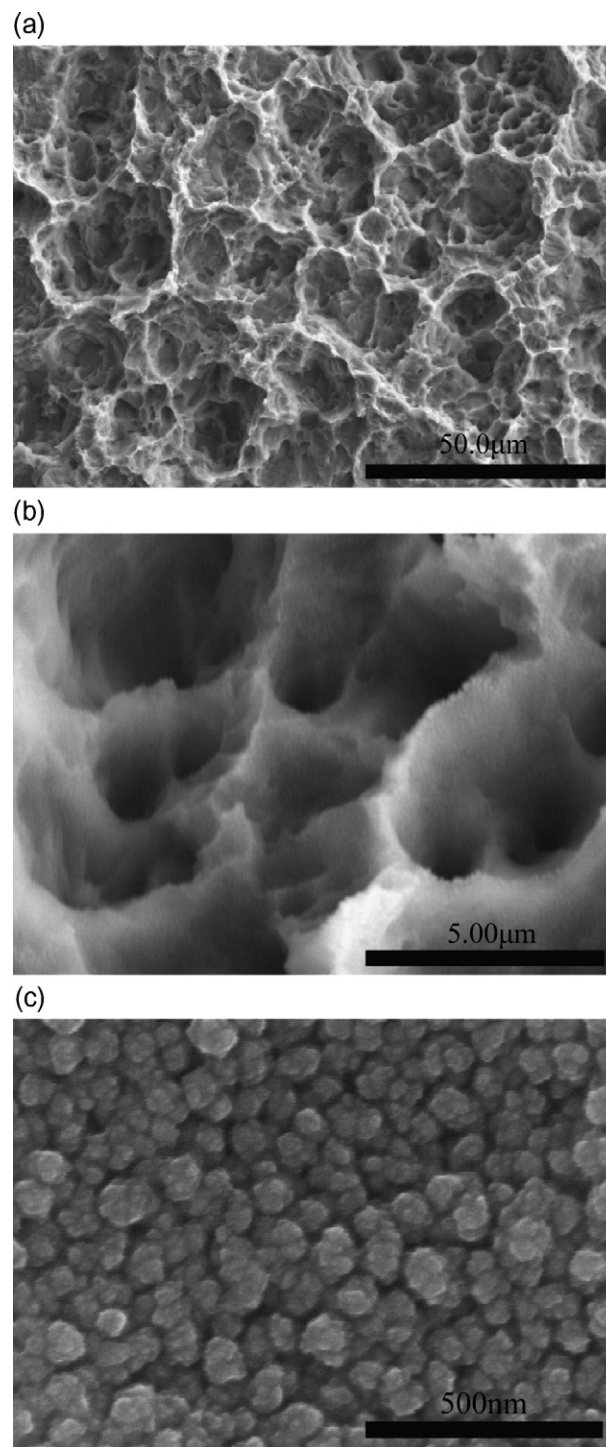


Fig. 1. SEM images of $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ films on Ti substrate with various magnifications.

the deposits have a very rough and alveolate network morphology. In addition, a highly three-dimensional porous outer structure is observed clearly for the $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ film on the exposed surface area of Ti substrate in Fig. 1(a) with low magnification. The $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ thin film possesses a micro-porous nature as shown in Fig. 1(b), which promotes ruthenium species within the $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ film to exchange protons more freely with the electrolyte during the Faradic redox transitions.

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