

Anodic, cathodic and cyclic voltammetric deposition of ruthenium oxides from aqueous RuCl_3 solutions

Jiin-Jiang Jow^{a,*}, Hung-Jie Lee^a, Ho-Rei Chen^a, Mao-Sung Wu^a, Tsong-Yang Wei^b

^a Department of Chemical and Material Engineering, National Kaohsiung University of Applied Sciences, Kaohsiung 80782, Taiwan

^b Institute of Nuclear Energy Research, Atomic Energy Council, Taoyuan 32546, Taiwan

Received 26 May 2006; received in revised form 5 September 2006; accepted 5 September 2006

Available online 17 October 2006

Abstract

Anodic, cathodic and cyclic voltammetric (CV) deposition of ruthenium oxides from aqueous RuCl_3 solutions have been investigated using stationary and rotating disk electrodes (RDE) in this work. The CV deposition behavior was examined using a RDE to differentiate the contribution of current from the reactions of ruthenium ions in the electrolyte and ruthenium oxides already adsorbed on the electrode. The results indicate that the CV growth of ruthenium oxides within the potential range of aqueous electrolyte decomposition is attributed to the anodic oxidation of ruthenium ions in the electrolyte. Cathodic deposition occurs only at potential negative than -0.30 V versus saturated calomel electrode (SCE) when H_2 evolves on the electrodes. Anodic deposition of ruthenium oxides can be obtained effectively in the potential range of ca. 0.9 – 1.1 V versus SCE, depending on the pH value of the electrolyte. The optimum anodic and cathodic deposition potential for maximum deposition efficiency is 1.0 and -0.9 V versus SCE, respectively, in the electrolyte solution of pH 2.

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Keywords: Ruthenium oxides; Cyclic voltammetric deposition; Rotating disk electrode; Anodic deposition; Cathodic deposition

1. Introduction

In recent years, the preparation of ruthenium oxide films has attracted considerable attention in view of their potential application in electrochemical capacitors [1–4], and electrochemical sensors [5,6]. Various methods, such as solution chemistry techniques [1,7], electrochemical deposition [1,7–21], sputtering techniques [6,7], and organometallic chemical vapor deposition [22] have been employed to prepare ruthenium oxide films. The electrodeposition methods offer a number of advantages compared with other techniques. For instance, the preparation procedure is relatively simple, and the growth of film can be easily modulated by varying the experimental parameters, such as applied potential, electrolyte compositions and deposition time.

Electrodeposition methods for preparing ruthenium oxide films, including cathodic [8–15], anodic [16] and cyclic voltammetric (CV) depositions [17–21] have been widely studied.

Lietzke and Griess [13] investigated the cathodic deposition from very dilute RuNOCl_3 solution at various metal substrates and found that the discharge of hydrogen is of importance in the cathodic deposition of ruthenium. Zhitomirsky et al. [9,10] studied the cathodic deposition from RuCl_3 aqueous solution and pointed out that the deposition is due to the reactions of ruthenium ions with the electrogenerated base on the electrode, similar to the wet chemical method of oxide powder processing. However, cathodic depositions carried out in various electrolyte solutions showed very low deposition efficiencies. The composition of cathodic deposits reported were $\text{Ru}(0)$ and ruthenium oxides. On the other hand, Anderson et al. deposited ruthenium oxide films anodically at 0.9 V versus SCE in the aqueous solution of benzeneruthenium(II)-aqua complex on a RDE, and pointed out that the deposits are highly redox reversible hydrous ruthenium oxides and tending to dissolve into the electrolyte [16]. However, studies on the anodic deposition of ruthenium oxides have been scarce. In addition to the cathodic and anodic methods, CV methods have also been used for depositing ruthenium oxide films [17–21] with advantageous results, particularly for supercapacitor electrodes since high charge storage capacity can be obtained simply by increasing the number

* Corresponding author. Tel.: +886 7 3814526x5109; fax: +886 7 3830674.
E-mail address: jjjow@cc.kuas.edu.tw (J.-J. Jow).

of cycles. The CV deposition methods were carried out by anodic/cathodic cycling within the decomposition potential of aqueous electrolyte solution. The oxidation and reduction of ruthenium ions in the electrolyte as well as the already deposited ruthenium oxides on the electrode substrate occur repetitively during the anodic/cathodic cycling procedures. However, the contributions of anodic and cathodic reactions to the growth of ruthenium oxides during CV cycling remain unclear. Therefore, it is significant to clarify the anodic and cathodic reactions for the development of electrochemical deposition methods.

In this work, CV, cathodic and anodic depositions of ruthenium oxides from aqueous RuCl_3 solutions have been studied systematically. The CV deposition behavior was analyzed using a RDE to reveal the contributions of anodic and cathodic reactions of ruthenium ions to the growth rate of ruthenium oxides during the CV procedures. The anodic and cathodic deposition efficiencies on stationary substrates under various depositing conditions were investigated and the optimum deposition conditions for maximum deposition efficiency were explored. The ruthenium oxide films prepared by the various electrochemical methods were characterized by X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM) to reveal the differences between the deposits.

2. Experimental

The electrochemical experiments were carried out on a potentiostat/galvanostat (Autolab-PGSTAT30 Eco Chemie) in a divided H-cell separated with a Nafion membrane. A platinum spiral wire with surface area of ca. 3.0 cm^2 was used as the counter electrode, and a SCE was used as the reference. The titanium RDE was prepared by replacing the Pt substrate on a Metrohm-628 RDE (Metrohm Ltd., Switzerland) by a Ti foil (99.7%, Aldrich) of 0.127 mm thick and 0.90 cm diameter. The Ti substrates were abraded with ultra fine abrasive paper (Fuji Star 600 CCCw, Japan), degreased with cathodic treatment in 0.5 M H_2SO_4 at 5.0 mA for 30 s and washed with distilled water before electrochemical depositions.

Nitrogen gas was employed to purge the dissolved oxygen in the distilled water for preparing electrolyte solution and to separate air from the electrolyte solutions during the experiments. The electrolyte solutions containing 10 mM $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (Riedel-deHaën) in 0.1 M KCl were prepared and kept in nitrogen atmosphere for 2 days before measurements were made. An adequate amount of fresh electrolyte solution in the divided H-cell was used for each experimental run to avoid the effect of changes in electrolyte composition owing to anodic or cathodic reactions.

The pH value of the electrolyte solutions was adjusted with HCl or KOH aqueous solution. Experiments were conducted at ambient laboratory temperature of $26 \pm 1 \text{ }^\circ\text{C}$.

The SEM pictures of the films were obtained on the JEOL-5601 scanning electron microscope. The XPS spectra were obtained at pressure of 1.0×10^{-10} mbar on a VG ESCA Scientific Theta Probe (2002) using monochromatic Al $\text{K}\alpha$ radiation (1486.6 eV).

3. Results and discussion

3.1. CV deposition of ruthenium oxide films—contribution of anodic oxidation and cathodic reduction of Ru(III) ions in the CV procedures to the growth rate of ruthenium oxide films

The dependence of ruthenium oxide growth rate on the anodic oxidation and cathodic reduction of ruthenium ions in the CV procedures were performed via changing the rotating rate (RR) of RDE from 500 to 2000 rpm between ca. 0.65 to 1.05 V and 0.25 to -0.15 V versus SCE, respectively.

Fig. 1A depicts the CV behavior of ruthenium oxide growth on the RDE with RR increased in the sixth to eighth cycles from 500 to 2000 rpm between ca. 0.65 and 1.05 V versus SCE. The anodic current between 0.65 and 1.05 V versus SCE shifts upwards in response to the increase in RR. On the other hand, Fig. 1B presents the CV behavior of ruthenium oxide growth on the RDE with RR changed in the 7–10th cycles from 500 to 2000 rpm between ca. 0.25 and -0.15 V versus SCE. The cathodic current between 0.25 and -0.15 V versus SCE shifts

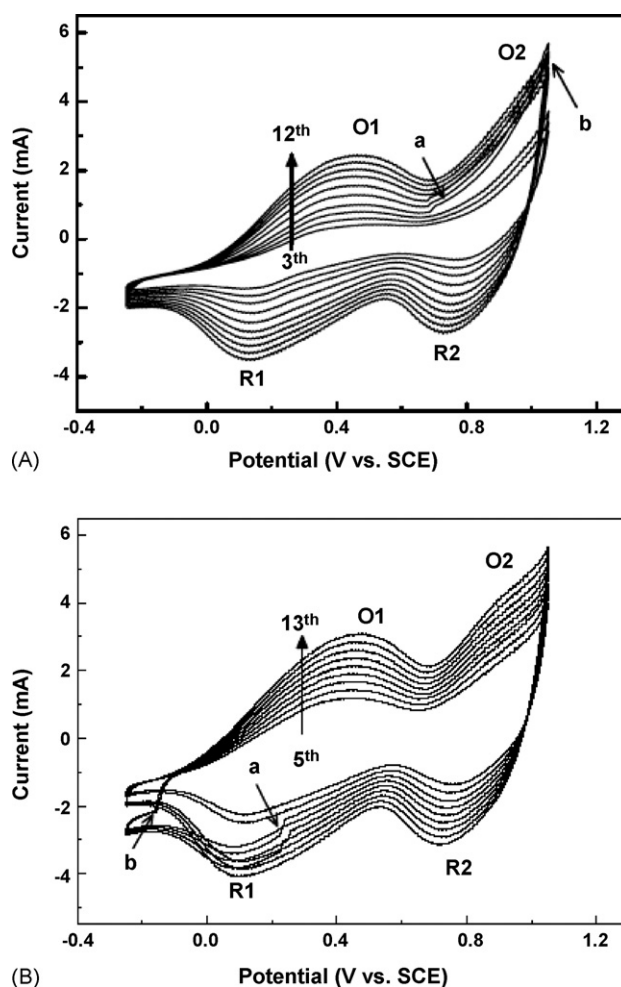


Fig. 1. CV behavior of ruthenium oxides growth on a RDE with rotating rate changed from 500 to 2000 rpm between ca. (A) 0.65 and 1.0 V, (B) 0.25 and -0.15 V versus SCE in some of the cycles during CV procedures. pH 2.0; scan rate 50 mV s^{-1} .

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