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Electrodeposited ruthenium oxide thin films for supercapacitor: Effect of surface treatments

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ABSTRACT

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Keywords: Ruthenium oxide Supercapacitor Surface treatment Contact angle Surface morphology Amorphous and porous ruthenium oxide thin films have been deposited from aqueous Ru(III)Cl₃ solution on stainless steel substrates using electrodeposition method. Cyclic voltammetry study of a film showed a maximum specific capacitance of 650 F g⁻¹ in 0.5 M H₂SO₄ electrolyte. The surface treatments such as air annealing, anodization and ultrasonic weltering affected surface morphology. The supercapacitance of ruthenium oxide electrode is found to be dependent on the surface morphology.

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1. Introduction

Supercapacitor is similar to a regular capacitor in operation; however, it offers a very high capacitance in a small package for achieving the requirement of power supplies. A material to be a potential candidate for supercapacitor should be able to get oxidized and reduce reversibility between various oxidation states [1,2]. The examples include transition metal oxides and conducting polymers [3–6]. Ruthenium oxide ($RuO_2 \cdot xH_2O$) is a mixed electronic–protonic conductor which has been reported to be the most promising materials for supercapacitor [7,8]. Amorphous $RuO_2 \cdot xH_2O$ formed by sol–gel process is reported to exhibit high specific capacitance [7].

Recently, electrodeposition method has been developed to replace sol–gel process [2,8,9]. The maximum specific capacitance of 788 F g⁻¹ has been reported for galvanostatically deposited RuO₂ thin films [10]. Several studies are reported to improve the specific capacitance of ruthenium oxide. The specific capacitance of ruthenium oxide has been enhanced by surface treatments like annealing in air [7,11] and electrochemical anodization in aqueous

media [12] or by ultrasonic weltering in NaOH [13]. Although, in these studies specific capacitance is improved, the reproducibility for obtaining high specific capacitance was not good. Further, the improvement in capacitance is strongly dependent on method of preparation and related structure of material [7,11–15].

In present study, ruthenium oxide electrodes are prepared by cathodic electrodeposition on stainless steel substrate. The cyclic



Fig. 1. Scanning electron micrograph (SEM) of $RuO_2\ film$ for 0.349 mg $cm^{-2}\ film$ thickness.

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Fig. 2. Cross-section of the as-deposited ${\rm RuO_2}$ film. Inset shows the dense layer of ${\rm RuO_2}$ film.

voltammetric study is carried out to find the capacitive performance of ruthenium oxide electrode. The effect of surface treatments such as air annealing, anodization and ultrasonic weltering on the supercapacitance is studied.

2. Experimental

Ruthenium oxide films were electrodeposited from RuCl₃:xH₂O aqueous solution using potentiostat (EG&G PAR 263-A model) at 333 K bath temperature. Graphite plate and saturated calomel



Fig. 3. Water contact angle before the surface treatment.

electrode (SCE) were used as a counter and reference electrodes, respectively. The cathodic electrodeposition was performed at -0.45 V/SCE potential. Prior to the deposition, the substrates were polished with zero grade polish paper and ultrasonically cleaned with double distilled water.



Fig. 4. (a) Morphology of RuO₂ film after annealing. (b) The cross-section of the annealed RuO₂ film. Inset shows the porous structure. (c) The contact angle after annealing. (d) Cyclic voltammogram of RuO₂ film electrode (i) before and (ii) after annealing.

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Effect	of surface	treatments	on valı	ues of	specific	capacitance.

Sr. no.	Surface treatment	Sample weight (mg cm ⁻²)	Contact angle (°)	Specific capacitance (F g ⁻¹)
1	As-deposited	0.349	~83.9	650
2	Annealing (473 K, 2 h)	0.349	\sim 70.9	111
3	Anodization (0.1 M H_2SO_4 at +1.2 V/SCE, 1.5 h)	0.349	~10.7	70
4	Ultrasonic weltering (1 M NaOH, 30 min)	~0.349	~ 6.5	14

After deposition, the electrodes were dried in air. The amount of ruthenium oxide deposited was measured by weighing the difference between bare electrode before and after deposition. The surface morphology of films was examined using a scanning electron microscope, Cambridge Stereoscan 250 MK-3 unit. The wettability study was carried out using contact angle measurement based on sessile drop method, which consists of observing the water drop through a microscope compiled to a goniometer (Phoenix 150, Surface Electro Optics, Korea). The 2 mL drops of water were sequentially deposited at different surface positions on film using Pame-Hart Inc. model-10 microsyringe.

Electrochemical measurements for supercapacitor study were carried out in $0.5 \text{ M} \text{ H}_2\text{SO}_4$ electrolyte using three-electrode electrochemical cell, in which RuO_2 thin film electrode was used as a working electrode, platinum as a counter electrode, and saturated calomel electrode (SCE) as a reference electrode.

Further, the effect of surface treatments on supercapacitive performance was studied on three identical electrodes with maximum specific capacitance. The electrodes were annealed, or anodized or ultrasonically weltered. The surface morphology, contact angle and supercapacitive studies of these electrodes were carried out.

3. Results and discussion

3.1. Characterization of RuO₂ films

Samples with 1 cm \times 1 cm surface area were prepared using electrodeposition method. Since deposited films were found to be porous, the accurate measurement of film thickness was not possible [10]. Therefore deposited weight (mg cm^{-2}) of a RuO₂ film on substrate was measured in place of film thickness. The X-ray diffraction (XRD) (not shown) study depicted that films are amorphous.

Scanning electron microscopy (SEM) analysis was done to study the morphology of the RuO_2 film. The SEM in Fig. 1 shows that the film consists of a dense layer covered by agglomeration of particles forming a porous structure. Fig. 2 shows the cross-section of asdeposited RuO_2 film. A dense layer of as-deposited film is revealed on further magnification (inset, Fig. 2). Fig. 3 shows the contact angle measurement of as-deposited RuO_2 film. The contact angle of 83.9° is an indication of hydrophilic behavior.

3.2. Supercapacitance study of RuO₂ films

The supercapacitive properties of as-deposited RuO_2 films were studied using cyclic voltammetric (CV) in 0.5 M H_2SO_4 electrolyte.



Fig. 5. (a) Morphology of RuO₂ film after anodization. (b) Cross-section of the anodized RuO₂ film. Inset shows the porous structure. (c) Contact angle after anodization. (d) Cyclic voltammogram of RuO₂ film electrode (i) before and (ii) after anodization.

The potential range between -100 and +600 mV/SCE was used with a scanning rate of 20 mV s⁻¹. It was found that RuO₂ electrode with 0.349 mg cm⁻² film thickness possesses high specific capacitance of 650 F g⁻¹. Such a high value of specific capacitance on stainless steel electrode was achieved due to the amorphous and porous nature of deposited material [16,17]. This value is comparable with value of capacitance (788 F g⁻¹) obtained for electrodeposited RuO₂ film on titanium substrate [11].

3.3. Effect of the surface treatments on the supercapacitive performance

The effect of surface treatments on the supercapacitive performance was studied. The electrode with maximum specific capacitance (650 F g⁻¹) was cut into three identical electrodes. The first RuO₂ electrode was annealed in air at 473 K for 2 h in a tube furnace. For second electrode, the anodization treatment was carried out in 0.1 M H₂SO₄ at +1.2 V/SCE for 1.5 h and third electrode was ultrasonically weltered in 1 M NaOH for 30 min using ultrasonic cleaner. In case of ultrasonically weltered sample, a negligible weight loss (0.000002 g) was observed.

3.3.1. Effect of air annealing

The morphology of RuO₂ film is porous with hydrophilic nature (Fig. 4). After annealing, the spherical particles became blurred and porosity increased because of reconstruction of particles as shown in Fig. 4(a). The cross-section of annealed film is shown in Fig. 4(b). The inset also supports the increased porosity after annealing. The decreased contact angle from 83.9° to $\sim 70.9^{\circ}$ (Fig. 4(c)) shows increased hydrophilic nature of film after annealing.

The CV performance of annealed electrode was studied. The CV (Fig. 4(d)) shows that specific capacitance decreases from 650 F g⁻¹ to 111 F g⁻¹ after annealing. Such reduction in specific capacitance was due to the loss in hydrous content of RuO₂ electrode [15]. It is also noted that, after surface treatment film becomes more porous, which may offer some contact resistance to charge carrier between substrate and electrode material resulting in different shape of CV from original one. As seen from Table 1, after annealing RuO₂ electrode exhibits significant reduction in supercapacitive value.

3.3.2. Effect of anodization and ultrasonic weltering

The performance of RuO₂ electrode was studied after anodization and ultrasonic weltering. The SEM (Fig. 5(a)) shows that the particles are well distinguished from each other indicating that growth of particles took place from all sites after anodization. The cross-section in Fig. 5(b) displays that the morphology becomes more porous after anodization and hence decrease in water contact angle. Fig. 5(c) shows the contact angle of 10.7° for anodized film. From CV studies (Fig. 5(d)), it is observed that specific capacitance decreases to 70 F g⁻¹ after anodization.

In case of ultrasonically weltered film, the hydrophilic nature changed to super-hydrophilic one (Fig. 6(a)) with contact angle of 6.5° . From cross-section of sample (Fig. 6(b)), it is observed that film becomes much porous after ultrasonic weltering. Specific capacitance is decreased (Fig. 6(c)) to 14 F g^{-1} due to surface modification (not shown). Slight loss in mass of deposited film was observed after ultrasonic treatment due to the removal of unbound surface particles. Table 1 shows the summary of the results.

The stability of electrodes was tested in 0.5 M H_2SO_4 electrolyte at 20 mV s⁻¹ scan rate. It is observed that as-deposited electrodes show almost the same value of specific capacitance after 1000 cycles (not shown). Similarly, for surface treated electrodes, the value of specific capacitance was decreased after such scanning cycles indicating instability of treated electrodes.

In short, surface treatment strongly affects supercapacitance value, mainly due to the change in surface morphology. Increased



Fig. 6. (a) The contact angle after ultrasonic weltering. (b) Cross-section of the ultrasonically weltered film. Inset shows the porous structure. (c) Cyclic voltammogram of RuO_2 film electrode after ultrasonic weltering.

porosity after surface treatments results in decrease in contact angle. This indicates the decrease of hydration and increase in surface energy of thin films. As the surface energy inversely depends on contact angle, it is more for small contact angle. It is found that specific capacitance and contact angle of RuO₂ electrode decrease after surface treatments.

4. Conclusions

Electrodeposited RuO_2 thin films showed highest specific capacitance of 650 F g⁻¹ on stainless steel substrate. The surface treatments to RuO_2 films resulted in increased porosity. Therefore,

after surface treatments values of supercapacitance and contact angle are decreased.

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