Electrodeposited ruthenium oxide (RuO_2) films for electrochemical supercapacitors

BONG-OK PARK
University of Sogang, Seoul, Korea

C. D. LOKHANDE
Eco-Nano Research Center, Korea Institute of Science and Technology, P.O. Box 131, CheongRyang, Seoul, Korea

HYUNG-SANG PARK
University of Sogang, Seoul, Korea

KWANG-DEOG JUNG, OH-SHIM JOO*
Eco-Nano Research Center, Korea Institute of Science and Technology, P.O. Box 131, CheongRyang, Seoul, Korea

Ruthenium oxide (RuO_2) has been widely used because of its good catalytic properties in electrochemicals (e.g., chlorine and oxygen evolution) and photochemical (water decomposition) properties, and also in high charge storage capacity devices [1–3]. Use of RuO_2 as an electrode material in electrochemical capacitors has many advantages. RuO_2 has a high capacitance of the order of 150 to 250 microfarad/cm^2, which is about ten times higher than that of carbon. Such a high value is believed to be due to pseudocapacitance from surface reaction between Ru ions and H ions. The cyclic voltammetry curve of RuO_2 in an H_2SO_4 electrolyte is mirror—like and mainly featureless within a potential range of 1.4 V. Because of these properties, RuO_2 is considered attractive material for electrochemical capacitors [4]. Even though RuO_2 has a great advantage in terms of a wide potential range of highly reversible redox reactions with high specific capacitance, it is somewhat expensive for commercial electrodes in bulk, like electrochemical capacitors. Therefore, it is desirable to develop a thin film process for the preparation of RuO_2 electrode in order to reduce the cost of capacitor electrodes.

Ruthenium oxide thin films have been prepared using various techniques, including reactive sputtering [5], organometallic chemical vapor deposition [6], sol gel [1, 2, 7], electrodeposition [8–11] etc. Out of these, electrodeposition is a candidate method for the deposition of RuO_2 films. It offers rigid control by film thickness, uniformity, and deposition rate and is especially attractive owing to its low equipment cost and starting materials. Due to the use of an electric field, electrodeposition is particularly suited for the formation of uniform films on substrates of complicated shapes, impregnation of porous substrates and deposition on selected areas of the substrates [12]. The electrodeposition process is capable of forming thin films without the requirement of controlling atmosphere. The process is conducted at relatively low temperatures and therefore, in general, it results into an amorphous or nanocrystalline form of material. The amorphous or nanocrystalline form of ruthenium oxide is desired as it has a larger surface area than its crystalline form, which is essential for getting the high value of capacitance in electrochemical supercapacitors.

Cathodic electrodeposition of Ruthenium oxide thin films was carried out onto titanium substrates from an aqueous acidic ruthenium chloride ($RuCl_3{\cdot}xH_2O$) solution. A freshly prepared 0.04 molar solution was used. The deposition was carried out at 50 °C bath temperature. A platinum sheet was used as a counter electrode. Prior to deposition, titanium substrates (1×1 cm^2) were mechanically scrubbed by polish paper, degreased with soap and distilled water, and ultrasonically cleaned. A scanning potentiostat/galvanostat (E G & G PAR model-273A) was used in galvanostatic mode. Good quality RuO_2 films were deposited at current densities of 5.0 mA/cm^2 on titanium substrate. Depending upon film thickness, the deposition time period was varied between 30–210 min. After deposition, RuO_2 films were dried in a furnace at 373 K.

Thin films of RuO_2 were characterized using the following techniques. The X-ray diffraction (XRD) patterns were obtained by using X-ray diffractometer (RINT/PMAX 2500, Rigaku, Japan). Micro structural studies were carried out with scanning electron micrographs, obtained with FE-SEM, (SM-6340F, Jeol, Japan). The electrochemical capacitance study of RuO_2 electrode was carried out using a conventional three-electrode system using Pt counter electrode (2×2 cm^2 area) and Ag/AgCl reference electrode. The cyclic voltammogram (CV) curves were obtained in the 0.5 M H_2SO_4 solutions using scanning potentiostat. For charge-discharge studies of RuO_2 electrode, a unit cell was assembled with positive and negative electrodes, which were kept apart by the polypropylene separator. The unit cell was immersed in the 0.5 M H_2SO_4 solution and the galvanostatic charge-discharge test was

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*Author to whom all correspondence should be addressed.

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performed using automatic battery cycler (WBCS 3000) at a current of 3 mA in the voltage range of 0 to +0.8 V.

It was pointed out that electrodeposition is similar to the wet chemical method of oxide powder processing, making use of an electrogenerated base instead of alkali [8, 9, 13]. In the deposition from an aqueous bath the following reactions are considered to generate base at an electrode surface:

$$O_2 + 2H_2O + 4e^- \leftrightarrow 4OH^- \quad (1)$$

and,

$$2H_2O + 2e^- \leftrightarrow H_2 + 2OH^- \quad (2)$$

These reactions consume H_2O, generate OH^- and increase pH at the cathode. In electrodeposition, metal ions or complexes are hydrolyzed by electrogenerated base to form oxide, hydroxide or peroxide deposits on cathodic substrates. Hydroxide and peroxide deposits can be converted into corresponding oxides by thermal treatment. Hydrolysis reactions result in

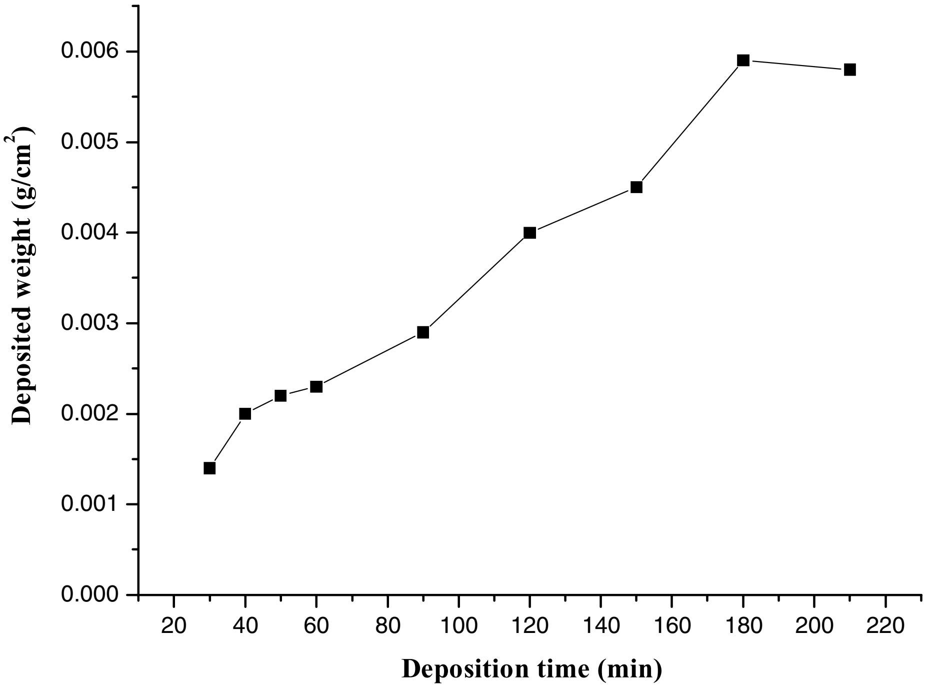


Figure 1 The variation of RuO_2 film weight (g/cm^2) on titanium substrate with deposition time period. The RuO_2 films were deposited at deposition current density of 5.0 mA/cm^2.

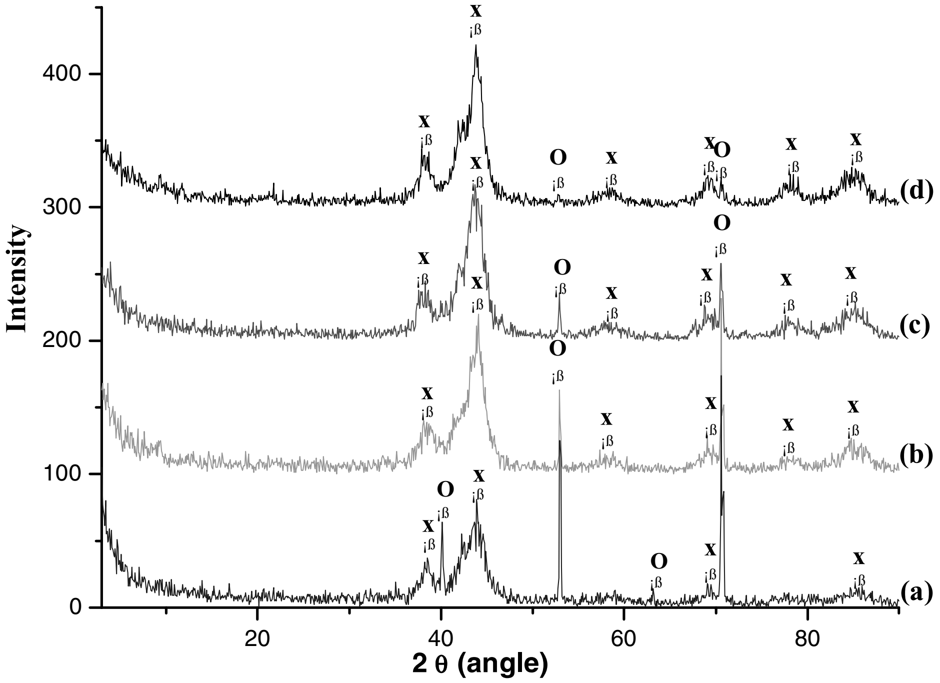
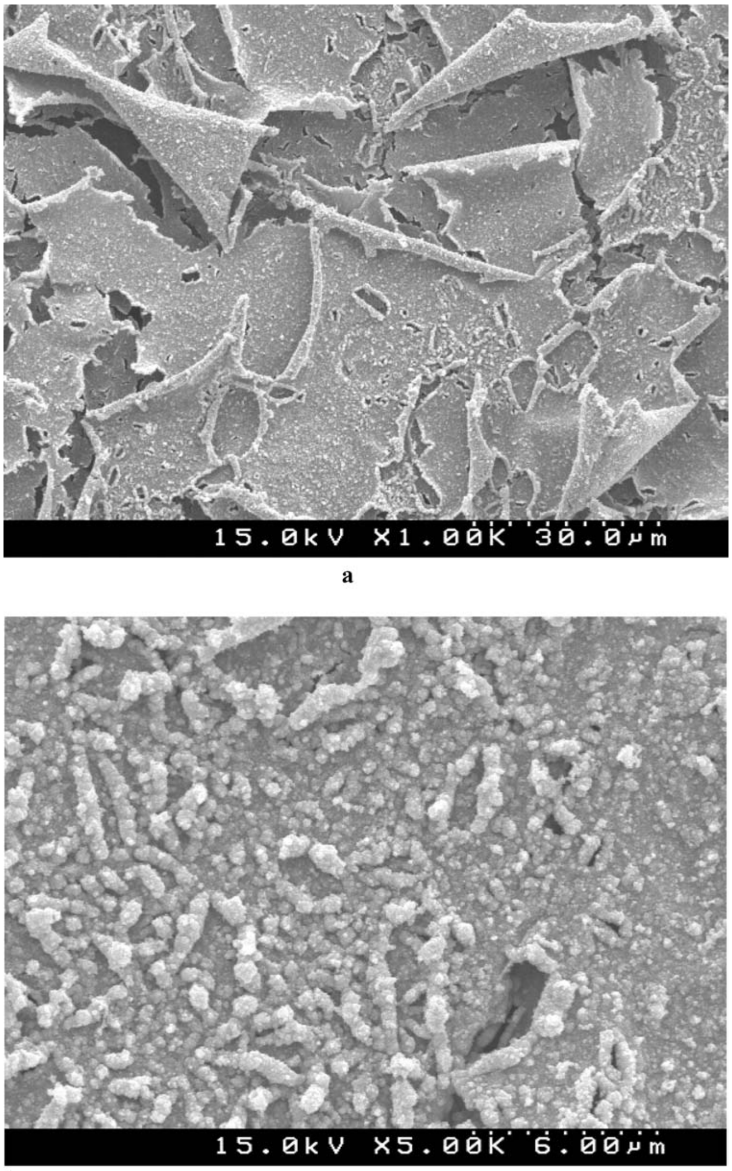


Figure 2 The scanning electron micrographs of RuO_2 films on titanium substrates at two different magnifications: (a) 1000× and (b) 5000×. The films were deposited for 30 min at 5.0 mA /cm^2 current density.

the accumulation of colloidal particles near the electrode and deposition is caused by flocculation introduced by the electrolyte. Recent studies have demonstrated the formation of RuO_2 powders by hydrolysis of $RuCl_3{\cdot}xH_2O$ in the presence of an alkali [14]. These results suggest the possibility of forming RuO_2 films by electrodeposition. The mechanism of RuO_2 deposition is not fully understood and it is thought to be performed via the hydroxide route. Hydrated ruthenium chloride is a heterogeneous ionic material with an average ruthenium oxidation state between 3 and 4 but closer to 4. For this reason, the mechanism of formation of RuO_2 from $RuCl_3{\cdot}xH_2O$ precursor is a complex one. The ruthenium species are most likely to precipitate as hydrated ruthenic oxide ($RuO_2{\cdot}xH_2O$) or ruthenic hydroxide $Ru(OH)_4$. This process consumes electrochemically generated OH^- ions [8, 9]. The electrodeposition potentials depend upon bath temperature, nature of substrate, metal ion concentration, complexing agent and its concentration etc.

The pH of $RuCl_3$ solution was varied in the range of 1.0 to 2.5 with the addition of hydrochloric acid solution. The suitable pH range was found to be 2.0 to 2.5. The deposition bath temperature was varied from 298 to 353 K. The suitable solution bath temperature was found to be 323 K, although RuO_2 films could be deposited in the above temperature range. The RuO_2 film thickness was increased by deposition for longer time periods. However, accurate RuO_2 film thickness measurement was not possible due to the high porosity of the films, therefore the deposited weight (g/cm^2) on the titanium substrate is considered instead of RuO_2 film thickness. Fig. 1 shows such a typical variation of RuO_2 film weight (g/cm^2) with the deposition time period. The deposited weight of RuO_2 film material was increased with the deposition time and maximum weight of 0.0059 g/cm^2 for the deposition period of 180 min was obtained. For further deposition period, the deposited weight showed a decline, probably due to the porous structure formation of RuO_2 film. The



a

b
5mA

Figure 3 The X-ray diffraction patterns of RuO_2 films deposited on titanium substrates for different time periods at current density of 5.0 mA/cm^2 (a) 30 min–0.0014 g/cm^2, (b) 60 min–0.0023 g/cm^2, (c) 120 min–0.0040 g/cm^2, and (d) 180 min–0.0059 g/cm^2. The marks ‘x’ and ‘O’ correspond to RuO_2 and Ti materials, respectively.

weight of RuO_2 film was typically between 0.0014 and 0.0059 g/cm^2, depending upon solution pH, bath temperature, deposition current density and time. The RuO_2 films were blackish in color.

The RuO_2 film crystallinity was analyzed using X-ray diffraction. The RuO_2 films with different weights were deposited by changing deposition time periods. In Fig. 2, X-ray diffraction spectra are shown corresponding to RuO_2 films of different weights on titanium substrates. The peak intensity of titanium substrate was reduced with the increasing thickness (weight/cm^2) of RuO_2 film. Practically, no difference was observed between XRD patterns corresponding to the different as-deposited RuO_2 films on the titanium substrates, which indicates the identical growth directions for RuO_2 films. The intensities of peaks corresponding to RuO_2 were increased with the increasing film weight. The peak corresponding to d-value of 2.05 Å could not be resolved well, as it can be attributed to both, deposition of metallic ruthenium or ruthenium oxide [15]. However, deposition of metallic ruthenium from aqueous bath is unlikely [8, 9] and therefore, the corresponding peak may be attributed to the RuO_2 [15]. The broadening of RuO_2 peaks suggests that the deposited RuO_2 consists of grains of nanometer size. The small grained or amorphous RuO_2 films have been also reported from cyclic voltametry method [16].

Scanning electron micrographs of RuO_2 film on titanium substrate at two different magnifications (1,000× and 5,000×) are shown in Fig. 3a and b. At 1000× magnification, RuO_2 film surface showed cracks and peeling off from the substrate. At high magnification (5000×), a RuO_2 film with porous structure is clearly visible, similar to those of other chemical methods such as cyclic voltametry [1, 16], sol–gel [2], spray pyrolysis [17] etc.

In case of RuO_2 based electrochemical supercapacitor, the capacitance comes mainly due to the pseudocapacitance of RuO_2 by surface redox reactions between electrolytes and RuO_2 electrode [1, 4]. The specific capacitance (F/g) is proportional to the specific surface area. Therefore, it is important to get more surface area of RuO_2 material. It is demonstrated that amorphous or nanocrystalline form of hydrous ruthenium oxide as an electrode has a much higher specific capacitance than that of the crystalline form of ruthenium oxide [10].

The electrodeposited nanocrystalline RuO_2 films were used in the formation of electrochemical supercapacitors and their performance was tested by studying CV curves and charge–discharge cycles. The CV curves showed that voltametric current decreases with increasing sweep cycles and stable currents are obtained after about 7–8 cycles. Fig. 4 shows the CV curves of RuO_2 thin films with different weights at scanning rate of 20 mV/sec. It is seen that voltametric currents gradually increased with film weight (g/cm^2) and showed capacitive behavior. Only some broad peaks were obtained and the CV curves are mainly featureless and indicated that this material is ideal for use as a capacitor electrode. The featureless curve is also indicative that the charge exchange between RuO_2 and electrolyte is independent of voltage [1].

From these data, capacitance was calculated for different weights of RuO_2 material deposited on titanium substrates, using the following relation:

$$C = I(A)/(\mathrm{d}V/\mathrm{d}t), \tag{3}$$

Where I is the average current in ampere and dV/dt is the voltage scanning rate. The specific capacitance of RuO_2 was obtained by dividing their respective weight. The variation of specific capacitance with deposited

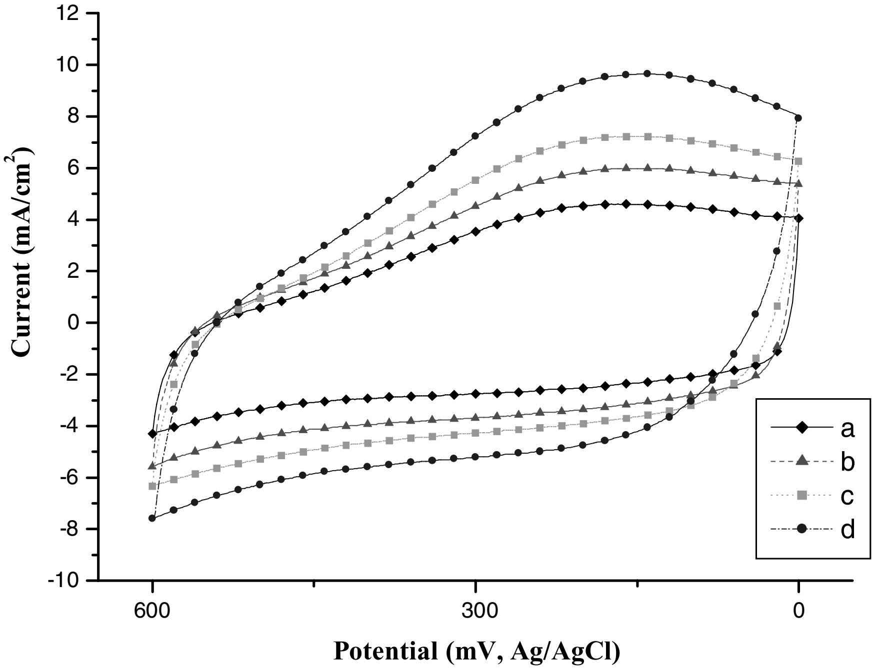


Figure 4 Cyclic voltammogram (CV) curves of RuO_2 films in 0.5 M H_2SO_4 electrolyte, deposited for different deposition time periods: (a) 30 min–0.0014 g/cm^2, (b) 60 min–0.0023 g/cm^2, (c) 120 min–0.0040 g/cm^2, and (d) 180 min–0.0059 g/cm^2. The scanning rate is 10 mV/sec.

weight of RuO_2 films showed the magnitudes as high as 788 F/g for the RuO_2 film deposited for 30 min (film weight, 0.0014 g/cm^2). This value is comparable to the values obtained with other methods of RuO_2 film deposition [1, 2, 11]. The charging-discharging behavior of electrochemical supercapacitor formed with RuO_2 electrode was studied. The behavior showed that RuO_2 electrodes are stable in the H_2SO_4 electrolyte.

In conclusion, using a simple cathodic electrodeposition method, RuO_2 films are deposited on titanium substrates. The RuO_2 films are nanocrystalline and porous. The supercapacitor studies based on nanocrystalline RuO_2 films showed that specific capacitance as high as 788 F/g is obtained, which is comparable with the values of other methods of RuO_2 film preparation.

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References

1. J. P. ZHENG, P. J. CYGAN and T. R. JOW, *J. Electrochem. Soc.* **142** (1995) 2699.
2. CHI-CHANG HU and K.-H. CHANG, *Electrochim. Acta* **45** (2000) 2685.
3. Y. U. JEONG and A. MANTHIRAM, *J. Electrochem. Soc.* **148** (2000) 189.
4. S. HADZI-JORDANOV, H. ANGERSTEIN-KOZLAWSKA, M. VUKOVIC and B. E. CONWAY, *ibid.* **125** (1978) 1471.
5. M. TAKEUCHI, K. MIWADA and H. NAGASAKO, *Appl. Surf. Sci.* **12/13** (1982) 298.
6. Y. S. HUANG and P. C. LIAO, *Solar Energy Mater. Sol. Cells* **55** (1998) 179.
7. Y. MURAKAMI, S. TSUCHIYA, K. YAHIKOZAWA and Y. TAKASU, *J. Mater. Sci. Lett.* **13** (1994) 1773.
8. I. ZHITOMIRSKY and L. GAL-OR, *Mater. Lett.* **31** (1997) 155.
9. I. ZHITOMIRSKY, *ibid.* **33** (1998) 305.
10. CHI-CHANG HU and K.-H. CHANG, *J. Power Sources* **112** (2002) 401.
11. S.-H. LEE, P. LIU, H. M. CHEONG, C. EDWIN TRACY and S. K. DEB, *Solid State Ionics* (2003) in press.
12. C. D. LOKHANDE and S. H. PAWAR, *Phys. Stat. Solidi* (a) **111** (1989) 17.
13. I. ZHITOMIRSKY and L. GAL-OR, *J. Europ. Ceram. Soc.* **16** (1996) 819.
14. I. ZHITOMIRSKY, *J. Mater. Sci.* **34** (1999) 2441.
15. JCPDS Data Card Nos. 021365 and 181139.
16. CHI-CHANG HU, Y.-H. HUANG and K.-H CHANG, *J. Power Sources* **108** (2002) 117.
17. J. H. KIM and K. B. KIM, *Electrochem. Solid-State Lett.* **4** (2001) A62.

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