

Short communication

## Performance of supercapacitor with electrodeposited ruthenium oxide film electrodes—effect of film thickness

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### Abstract

Thin-film ruthenium oxide electrodes are prepared by cathodic electrodeposition on a titanium substrate. Different deposition periods are used to obtain different film thicknesses. The electrodes are used to form a supercapacitor with a 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte. The specific capacitance and charge–discharge periods are found to be dependent on the electrode thickness. A maximum specific capacitance of 788 F g<sup>-1</sup> is achieved with an electrode thickness of 0.0014 g cm<sup>-2</sup>. These results are explained by considering the morphological changes that take place with increasing film thickness.

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**Keywords:** Ruthenium oxide; Electrodeposition; Supercapacitor; Thin-film electrode; Morphology

### 1. Introduction

Supercapacitors (or electrochemical) capacitors are symmetrical devices in which the electrolyte is placed between two identical electrode systems. While supercapacitors can store and deliver charge on a time scale of the order of several tens of seconds, their ability to deliver charge at short times is dictated by the kinetics of the surface redox (oxidation–reduction) reactions and the combined resistivity of the matrix and electrolyte [1]. Supercapacitors fall into two broad categories: (i) double-layer capacitors which rely solely on charge separation across the electrical double layer; (ii) pseudocapacitors that have enhanced charge storage (similar to a battery, but to a lesser extent) derived from faradaic charge transfer in parallel with the double-layer. The double-layer, created naturally at an electrode/electrolyte interface, has a thickness of about 10 Å. For an electrode with high area, the capacitance per unit geometric area is amplified by the roughness factor, which can approach 100 000 times. The specific capacitance is further increased in electrode systems that have a substantial potential region over which a faradaic reaction (similar to a battery reaction,

but to a lesser degree) can take place. Thus supercapacitors, unlike their electrostatic counterparts, can accumulate substantial charge, because of charge separation at the molecular level coupled with a high charge density associated with the surface redox processes on high-area electrodes [2].

In order to obtain a high level of stored energy per unit weight and volume, it is necessary to use electrochemically active materials of significantly higher energy content than those in present commercial capacitors. The most promising candidates are high surface-area activated carbon and metal oxides, such as RuO<sub>2</sub>. A RuO<sub>2</sub> electrode with a specific capacitance as high as 760 F g<sup>-1</sup> has been reported [3]. Furthermore, in order to access the entire porous structure of RuO<sub>2</sub> efficiently, and thereby achieve high capacitance (hence, high energy) and high power with a low electrochemical series resistance (ESR), the electrode has to be in the form of a thin film. Thin electrodes are more feasible with pseudocapacitors than with double-layer capacitors due to the greater capacitance density of the former. Even though RuO<sub>2</sub> has a great advantage in terms of a wide potential range of highly reversible redox reactions with high specific capacitance, it is somewhat expensive. Therefore, it is desirable to develop a process for the preparation of thin-film RuO<sub>2</sub> electrodes in order to reduce their cost as capacitor electrodes [4].

This investigation examines the dependence of supercapacitor performance on the thickness of RuO<sub>2</sub> film

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electrodes. The films are prepared by means of a cathodic electrodeposition method. Supercapacitor performance is assessed via cyclic voltammetry and charge–discharge studies.

## 2. Experimental

Ruthenium oxide thin films were electrodeposited on titanium substrates from an aqueous, acidic solution of ruthenium chloride ( $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ ) solution. A freshly prepared 0.04 M solution was used, and deposition was carried out at 50 °C. A scanning potentiostat/galvanostat (E G & G PAR model-273A) was used in galvanostatic mode to pass constant current of 5.0 mA cm<sup>-2</sup>. Depending on the desired film thickness, the deposition time period was varied between 30 and 210 min. After deposition, the RuO<sub>2</sub> films were dried in a furnace at 100 °C. Details of the experimental procedure and film characterization using various techniques are reported elsewhere [5].

Microstructural studies of RuO<sub>2</sub> films were carried out by means of scanning electron micrographs, which were obtained with a FE-SEM (SM-6340F, JEOL, Japan). Supercapacitance studies of the RuO<sub>2</sub> electrodes were performed in a conventional three-electrode system with a platinum counter electrode (2 cm × 2 cm area) and an Ag/AgCl reference electrode. Cyclic voltammograms (CV) were obtained in 0.5 M H<sub>2</sub>SO<sub>4</sub> using a scanning potentiostat. For charge–discharge studies of RuO<sub>2</sub> electrodes, a unit cell was assembled with positive and negative RuO<sub>2</sub> electrodes, which were kept apart by a polypropylene separator. The unit cell was immersed in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution and galvanostatic charge–discharge tests were performed using an Automatic battery cycler (WBCS 3000) at a current of 5 mA in the voltage range of 0 to + 0.8 V.

## 3. Results and discussion

Accurate measurement of the film thickness was not possible due to the high porosity of the films. Therefore, the weight of RuO<sub>2</sub> deposited (g cm<sup>-2</sup>) on the titanium substrate was taken as an indication of the film thickness [4]. The deposited weight of RuO<sub>2</sub> increased with deposition time and a maximum weight of 0.0059 g cm<sup>-2</sup> was obtained for a deposition period of 180 min. For longer deposition periods, the deposited weight declined. This is probably due to the porous structure of the RuO<sub>2</sub> film. Films with smaller thickness were found to be non-uniform. The weight of the RuO<sub>2</sub> film was typically between 0.0014 and 0.0059 g cm<sup>-2</sup>, depending on solution pH, the bath temperature, and the deposition current density and time. From X-ray diffraction studies, it was concluded that the deposited RuO<sub>2</sub> consisted of grains of nanometer size [5].

Cyclic voltammograms for RuO<sub>2</sub> film electrodes with different weights at a scanning rate of 10 mV s<sup>-1</sup> in the voltage range 0 to + 600 mV (versus Ag/AgCl) are shown in Fig. 1. The curves show that the current decreases with increasing sweep cycles and stable currents are obtained after about 7–8 cycles. The curves show capacitive behavior. Only some broad peaks are obtained and the curves are mainly featureless. Comparison of the curves reveals that the voltammetric current of RuO<sub>2</sub> electrode increases with film thickness, which indicates that the capacitance increases with increasing film thickness. Similar behaviour has been reported for RuO<sub>2</sub> films deposited by cyclic voltammetry [6], and sol gel [4] methods, and for a ruthenium oxide/carbon composite electrode [7].

From these data, the capacitance was calculated for different weights of RuO<sub>2</sub> material by means of the following

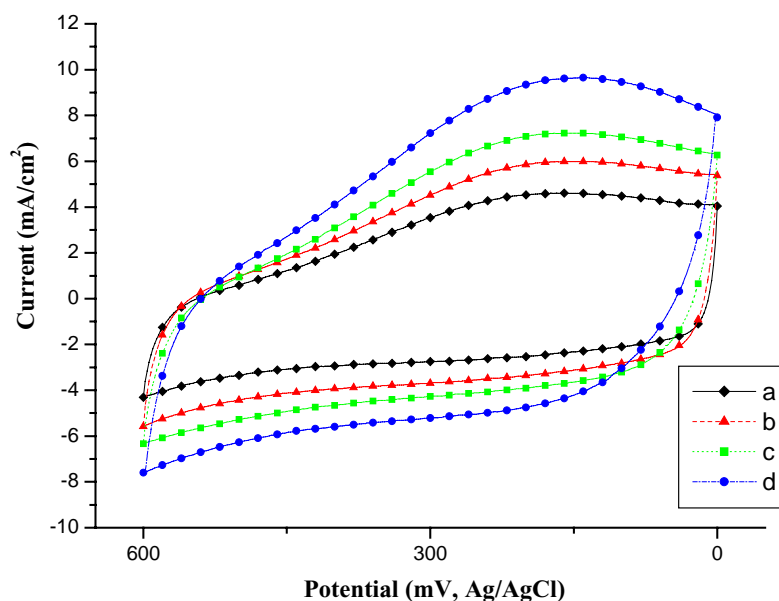


Fig. 1. Cyclic voltammograms for RuO<sub>2</sub> films in 0.5 M H<sub>2</sub>SO<sub>4</sub> film thickness: (a) 0.0014, (b) 0.0023, (c) 0.0040, and (d) 0.0059 g cm<sup>-2</sup>. Scanning rate is 10 mV s<sup>-1</sup>.

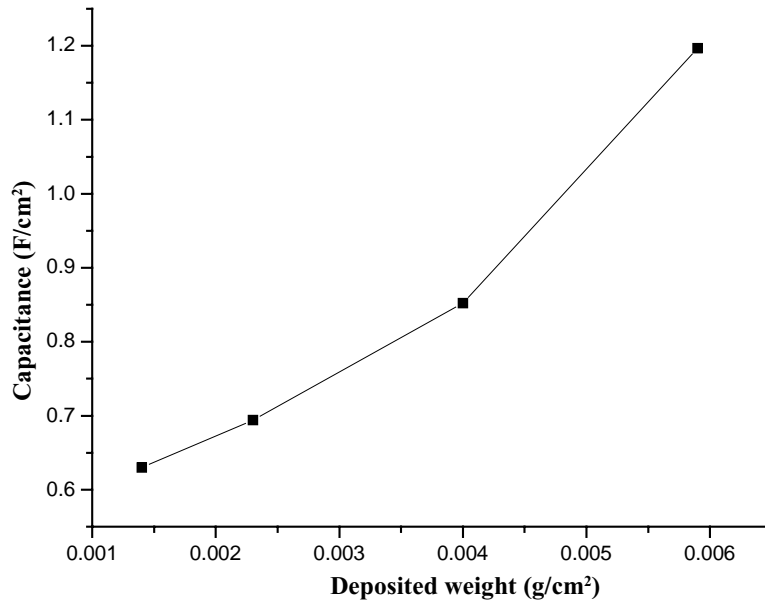


Fig. 2. Variation of capacitance (Fcm<sup>-2</sup>) with deposited weight (g cm<sup>-2</sup>) of RuO<sub>2</sub> electrode.

relation:

$$C = \frac{I}{dV/dt} \quad (1)$$

where  $I$  is the average current in amperes and  $dV/dt$  the voltage scanning rate. The variation in capacitance with deposited weight of RuO<sub>2</sub> is shown in Fig. 2. The value of capacitance increases from 0.62 to 1.92 F cm<sup>-2</sup> when the film thickness is increased from 0.0014 to 0.0059 g cm<sup>-2</sup>. This relationship indicates that the capacitance of RuO<sub>2</sub> coated electrodes arises mainly from the faradic reactions of elec-

troactive ruthenium species deposited on the substrate [8]. These values are higher than those reported by Fang et al. [9] for ruthenium oxide electrodes. This is believed to be due to: (i) the low temperature method of preparation and (ii) the high porosity of the RuO<sub>2</sub> material [5].

The variation of specific capacitance (F g<sup>-1</sup>) with RuO<sub>2</sub> film thickness is presented in Fig. 3. A maximum value of 788 F g<sup>-1</sup> is obtained for a film thickness of 0.0014 g cm<sup>-2</sup>. This value is comparable with those obtained with different methods for RuO<sub>2</sub> and carbon–RuO<sub>2</sub> composite thin electrode preparations [3,7]. The value of specific capacitance

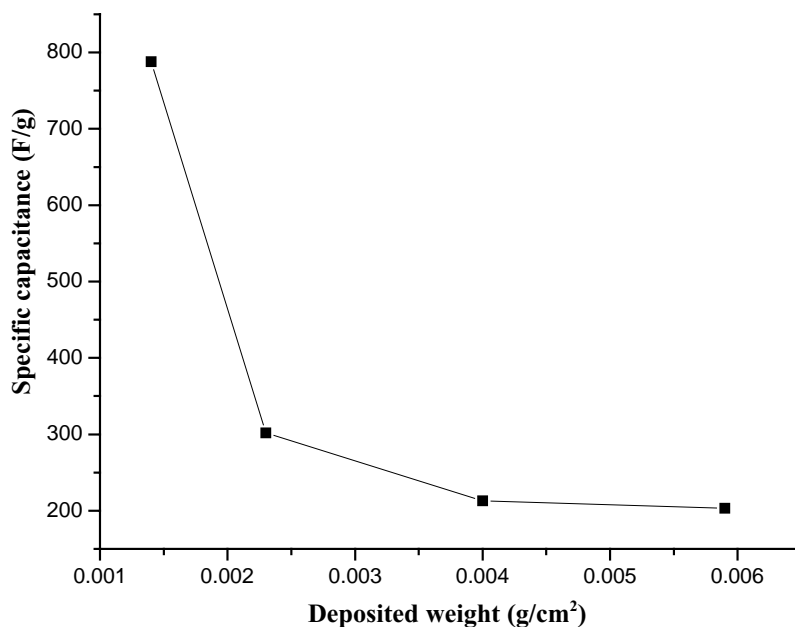


Fig. 3. Variation of specific capacitance (F g<sup>-1</sup>) with deposited weight (g cm<sup>-2</sup>) of RuO<sub>2</sub> electrode.

decreases drastically from 788 to 212 F gm<sup>-1</sup> with increase in film thickness from 0.0014 to 0.0059 g cm<sup>-2</sup>. The specific capacitance values for RuO<sub>2</sub> electrodes with thicknesses smaller than 0.0014 g cm<sup>-2</sup> could not be measured as these electrodes were found to be unstable in H<sub>2</sub>SO<sub>4</sub> electrolyte and results were not reproducible.

For a RuO<sub>2</sub>-based supercapacitor, the capacitance arises mainly from the pseudocapacitance of RuO<sub>2</sub> by surface redox reactions between the electrolyte and the RuO<sub>2</sub> electrode [1]. The specific capacitance (F g<sup>-1</sup>) is proportional to the specific surface area. Therefore, it is important to maximize the surface area of the RuO<sub>2</sub> material. The structural morphology of RuO<sub>2</sub> films of different thickness (g cm<sup>-2</sup>) were studied by means of scanning electron microscopy. The film morphology changes with different deposition periods. For a deposition period of 30 min (thickness: 0.0014 g cm<sup>-2</sup>), the surface of the RuO<sub>2</sub> film shows cracks and spalling from the titanium substrate; the surface has a ‘cracked-mud’ morphology. It is well known that oxide films obtained by thermal dehydration of hydroxides or peroxides exhibit cracking due to drying shrinkage—it is a common problem in wet chemical methods. With further deposition of ruthenium oxide films, the morphology changes from ‘cracked-mud’ to a round ‘cauliflower’ structure. Cracks are no longer visible for a deposition of 180 min (thickness: 0.0059 g cm<sup>-2</sup>). It is concluded that deposition of subsequent layers fills the defects that appeared after drying of the earlier layers. Scanning electron micrographs of RuO<sub>2</sub> films with thicknesses of 0.0014 and 0.0023 g cm<sup>-2</sup> are shown in Fig. 4(a) and (b), respectively. The micrographs show that a film with a small thickness has a highly porous outer structure. With increasing thickness, however, the outer surface becomes less porous without any visible cracks. Therefore, with

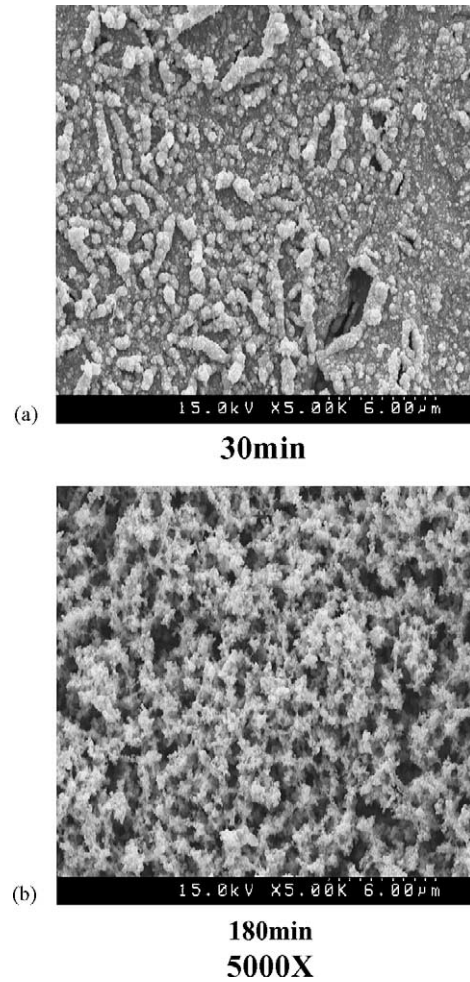


Fig. 4. Scanning electron micrographs (5000×) of RuO<sub>2</sub> films on titanium substrate. Film thickness: (a) 0.0014 and (b) 0.0023 g cm<sup>-2</sup>.

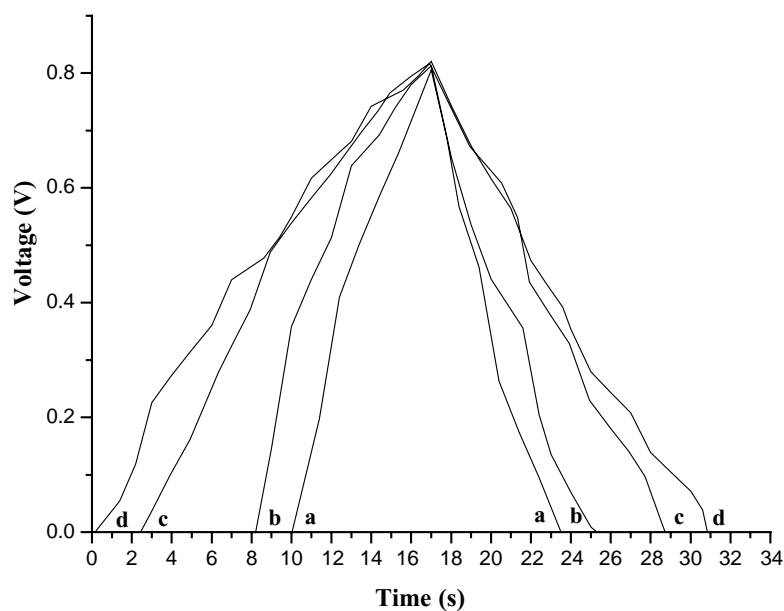


Fig. 5. Charge–discharge curves for supercapacitor with RuO<sub>2</sub> electrodes of thickness: (a) 0.0014, (b) 0.0023, (c) 0.0040 and (d) 0.0059 g cm<sup>-2</sup>.

increasing film thickness, the specific capacitance value decreases as the porosity decreases together with a change in surface morphology. Similar results have been reported for carbon–RuO<sub>2</sub> composite film electrodes [10].

The charge–discharge behaviour of RuO<sub>2</sub> electrodes with different thicknesses was studied by chronopotentiometry. Typical results in the potential range between 0 and 0.8 V in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 5 mA cm<sup>-2</sup> are given in Fig. 5. The absolute value of these curves {dV/dt}, decrease with increasing film thickness. As  $I/(dV/dt)$  is indicative of the capacitance of the oxide deposits, the average capacitance of every RuO<sub>2</sub> deposit can be calculated from the following relation:

$$\frac{I}{dV/dt} \simeq \frac{I}{\Delta V/\Delta t} \quad (2)$$

The average capacitance values are smaller (i.e., 0.41, 0.56, 0.70 and 0.80 F for a thickness of 0.0014, 0.0023, 0.004, 0.0059 g cm<sup>-2</sup>, respectively) than the values shown in Fig. 2. This is attributed to the additional electrochemical series resistance due to the polypropylene separator used in the experiment.

The energy efficiency of the capacitor was calculated as the ratio of the discharge and charge periods. The highest energy efficiency, 92%, was obtained for a film thickness of 0.0014 g cm<sup>-2</sup>. This value is close to that obtained (93%) for a RuO<sub>2</sub> electrode prepared by thermal decomposition [9]. The energy efficiency decreases with increasing film thickness. This result is similar to that found for loading RuO<sub>2</sub> in a carbon electrode [11].

#### 4. Conclusions

From the above results, it is concluded that a electrodeposited RuO<sub>2</sub> film can be used in the formation of supercapacitor. The highest value observed for the specific capacitance is 788 F gm<sup>-1</sup> for a RuO<sub>2</sub> film thickness of

0.0014 g cm<sup>-2</sup>. Even though the capacitance increases, the specific capacitance decreases with increasing film thickness. This is attributed to a decrease in the porosity of the outer layer and formation of a compact inner layer in the RuO<sub>2</sub> film with increasing thickness. The values of capacitance obtained from charge–discharge studies are small due to increased ESR through the presence of a separator. The energy efficiency decreases with increasing film thickness.

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