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Spin-Coated RuO_2 thin film Electrodes-Electrochemical performance with increasing deposition coats

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ABSTRACT

Thin-film ruthenium oxide electrodes were prepared by sol-gel spin coating technique on a stainless steel substrate. To obtain different film thicknesses deposition coats were increased. Thin films were used as electrodes for supercapacitor application with 0.1 M KOH electrolyte. Film thickness affected on the specific capacitance and charge–discharge. A maximum specific capacitance of 489 F/g was achieved with an electrode thickness of 0.1mg/ cm^2. These results were explained by considering the structural and morphological changes that take place with increasing film thickness. The energy efficiency decreased with increasing film thickness. RuO_2 film can withstand about 1000 cycles without a significant decrease in the capacitance. The EIS analysis data gave low value of ESR for 4 coats.

1.Introduction

Supercapacitors are the best candidates to provide the high power and long durability needed for the new energy devices [1]. The performance of supercapacitor is attributed to the high electrochemical reversibility of redox transitions within electrode materials [2-3]. Supercapacitor can store and deliver charge on a time scale of the order of several tens of seconds. Thus, they are becoming attractive energy storage devices particularly for high power requirements. Metallic oxides, conducting polymers have been generally used as electrode materials for supercapacitors [4-7]. Amongst these materials, Ruthenium oxide has been recognized as one of the most promising candidates for its good electrochemical capacitance performance and high specific capacitance. Since it is very expensive, many efforts are made to reduce the amount of ruthenium in the fabrication of supercapacitors [8]. In the present manuscript, we report the synthesis of ruthenium oxide thin films using sol-gel spin coating method on stainless substrate. The structural and morphological properties were presented for as deposited films.

2. Experimental

The ruthenium oxide thin films had been synthesized by a sol-gel spin coating technique. The detailed procedure for gel preparation was published elsewhere [9]. Stainless steel substrates with area equal to 1 cm^2 were used. The substrates were first polished by zero grade polish paper and cleaned by detergent, washed with double distilled water and dried at 100°C.Then the gel was deposited on the substrate by Spin coater unit.

To study the structural properties of the films, X-ray diffraction analysis was performed on a X-ray diffractometer D2 PHASER using CuKα radiation (λ= 1.54 A°).Surface morphology was examined using scanning electron microscope ((SEM JEOLJSM 6360). The electrochemical experiments were performed using a electrochemical workstation CH Instruments CH1608E. Measurements were carried out in a three-electrode cell equipped with a saturated calomel electrode (SCE) as reference, a Pt wire counter electrode and RuO_2 thin films of different loading weights as working electrode in 0.1 M KOH electrolyte.

3. Results and Discussions

3.1 Film formation

After the formation of gel by using spin coating method, thin and uniform films were synthesized on stainless steel substrate for spin rate of 3000 rpm and annealed at a temperature of 900°C. This resulted in the formation of well adherent and uniform ruthenium oxide thin films. The possible chemical reaction that takes place is

$$RuCl_3.nH_2O + (CH_3)_2CHOH \xrightarrow{\Delta} RuO_2 + CH_3CH_2OH + HCl \quad (1)$$

The process was repeated for multiple coats. Due to porosity, the weight of RuO_2 deposited on the SS substrate was taken as film thickness [10]. The deposited weight of RuO_2 increased with deposition coats and a maximum weight of 0.17 mg/cm^2 was obtained for 7 coats. It showed uniform, well adherent films from 4 to 7 deposition coats. The thickness of RuO_2 film was increased from 0.10 mg/cm^2 for 4 coats to 0.17 mg/cm^2 for 7 coats. The color of the film also changed with deposition coats. Initially the color was very light and turned darker with increasing mass. Fig. shows the variation of thickness of the film with coatings deposited. Films with smaller thickness were found to be non-uniform. For higher than 7 coats, it showed non-uniformly deposited and corrupted films.

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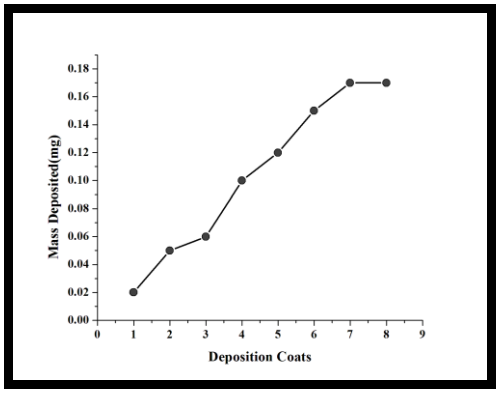

Figure 1. Variation of Thickness with Deposition Coats.

The formed ruthenium oxide thin films were blackish in color, uniform and well adherent to the substrate and were used for the further characterization.

3.2 Film Characterization:

3.2.1 Structural Characterization:

Film crystallinity was analyzed using X-ray diffraction. The XRD patterns of RuO_2 films on to the stainless steel substrate are shown in figure 2.

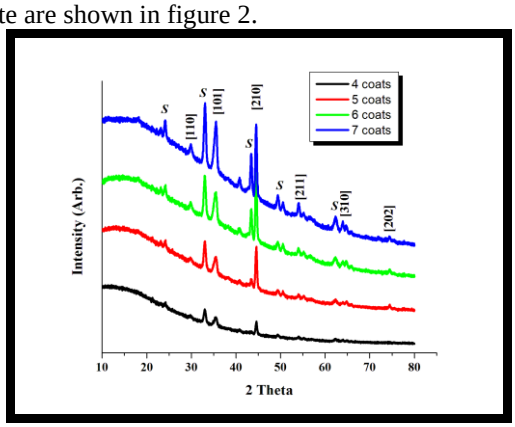

Figure 2.X-ray Diffractogram of RuO_2 thin films.

From XRD, it can be seen that for 4 coats, Bragg peaks were not comparatively dominant. After 4 coats, the intensity of the peaks was increased and also additional peaks of RuO2 were observed which confirmed the formation of oxide phase. The films for 4 coats showed comparatively less crystalline phase and this was confirmed by the relatively featureless diffraction peaks.Such phase obtained is feasible for supercapacitor application, since the protons can easily permeate through the bulk of the amorphous RuO2 electrode and whole amount of electrode is utilized for energy storage [11]. When the deposition layers were increased as 5, 6 and 7 coats, the XRD patterns have exhibited the characteristic peaks tending to ruthenium oxide at 30°, 35.1°, 45°, 54°, 65° and 75°. The intensity of the peaks increased with increasing deposition layers. The peaks which are labelled as 'S' correspond to stainless steel. The sharp intense peaks confirmed the crystalline nature and tetragonal structure of the ruthenium oxide (JCPDS Card Number 65-2824 and 88-0322).

3.2.2 Morphological Characterization:

The surface morphological study of the RuO_2 thin film has been carried out from SEM image. Fig 3. shows the SEM image of RuO_2 thin film on the steel substrate at magnifications X 5,000 and X 20,000 for 4th and 7th coat .It showed that the substrate is well covered with RuO2 material. In Fig. 3, random and rough traces were observed on stainless steel substrate. For 4 coats at higher magnification, smooth and fine features of RuO_2 material were observed which frequently indicates amorphous structure. The cracks on the film surface were increased with deposition layers. It was observed that clustering of more number of grains and grain size was increased with deposition layers.

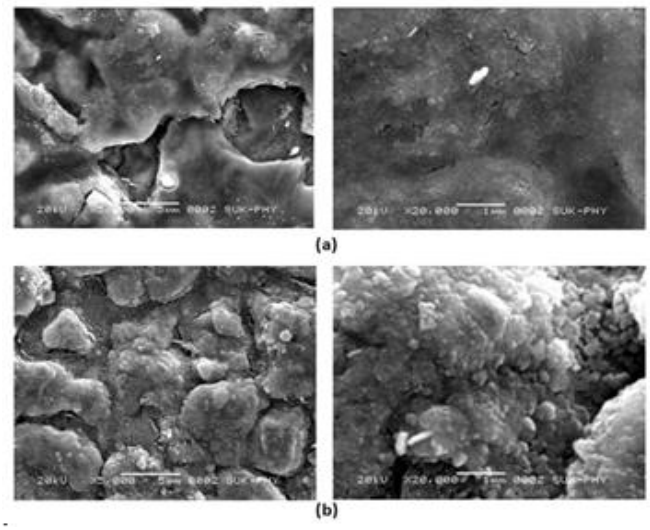

Figure 3. SEM images of RuO_2 thin films (a) 4 coats (b)7 coats for X 5000 and X20,000 magnification.

3.2.3 Electrochemical Performance

Cyclic Voltammetry was used to determine the electrochemical properties of the spin coated RuO_2 thin films. The electrode potential was scanned between -600 mV to 800 mV in both anodic and cathodic directions and current response was measured indicating the typical pseudocapacitive behavior. Fig 4. shows the C-V of ruthenium oxide electrode of different deposition layers in 0.1 M KOH electrolyte. The curves are mainly featureless. Further, the capacitive behavior of the oxide is enhanced as evidenced by the square like shape of the plot, which according to Conway [12] is a result of a nearly ideal capacitor. The current density increased with deposited mass which indicates that the capacitance increases with mass. Similar behavior has been reported for RuO_2 films deposited by sol-gel method [10].

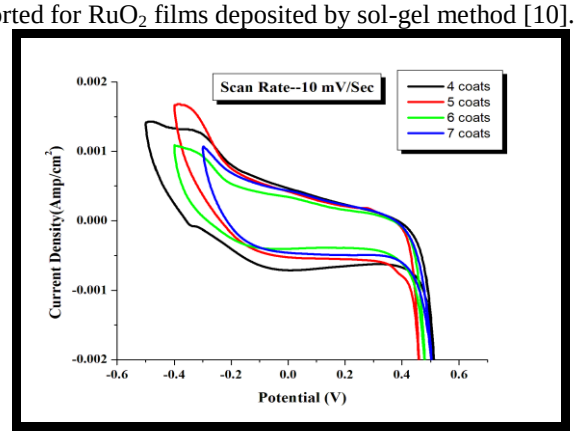

Fig 4. The cyclic voltammogram of RuO_2 thin films for 4 coats, 5 coats, 6 coats and 7 coats in 0.1 M KOH electrolyte for scan rate of 10 mV/Sec.

The specific capacitance of RuO_2 was calculated using the following equation:

$$C_S = \frac{1}{2mv(E_2 - E_1)} \int_{E_1}^{E_2} i(E)dE \qquad \text{---------- (1)}$$

where m is the mass deposited , v is potential scan rate, E_2 is higher potential cut off , E_1 is lower potential cut off and i(E) is current. As it includes both positive and negative scans, the factor 2 is used to correct the integrated area [13].The specific capacitance decreased with increase in deposition coats from 489 F/gm to 163 F/gm for 10 mV/sec scan rate. The possible reason for decrease in specific capacitance is the

crystalline nature of RuO_2 electrode. The rigid lattice of crystalline material causes to a difficulty to expand when the ions were inserted during redox reaction. Such type of decrease in specific capacitance with increase in deposited weight behavior is reported by Park et al. [14]. It has been reported that amorphous ruthenium oxide prepared by sol-gel process exhibits much superior performance as compared to crystalline RuO_2 [10]. The amorphous structure leads to fast proton diffusion rates thus contributing to a high specific capacitance [15]. The decrease of specific capacitance with increase of mass may be endorsed to the electrolyte diffusion boundaries in the pores due to increasing film thickness. The high specific capacitance for a mass of 0.10 mg /cm^2 (4 coats) possibly will be because of very thin film thickness, such that the redox reaction involves intact oxide particles. Specific capacitance also decreased with increase in scan rates for all thin films. Variation of capacitance and specific capacitance with thickness at scan rate of 10 mV/Sec is shown in figure 5.

During the oxidation and reduction process in RuO_2 , protons are exchanged with the electrolyte and electrode interface. Higher scan rates leads to either depletion or saturation of protons in the electrolyte within the electrode during the redox process as this proton transfer process is slow. This essentially results a decrease in capacitance of the electrode due to increase of ionic resistivity [16]. The lessening inclination of the capacitance shows that parts of the surface of the electrode are unapproachable at high charging-discharging rates.

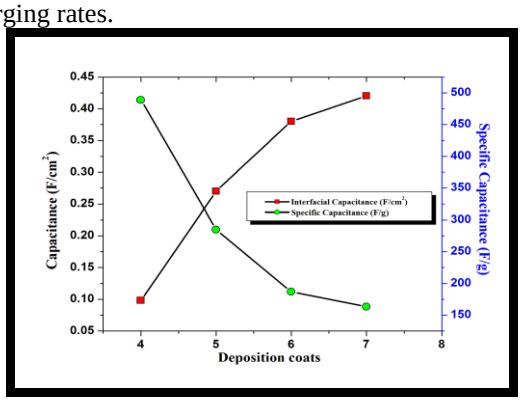

Fig 5 .Variation of Capacitance and specific capacitance with thickness at scan rate 10 mV/sec.

Hence, the specific capacitance obtained at the slowest scan rates is believed to be closest to that of complete use of the electrode material. Amorphous Ru oxides let the whole bulk of RuO2 to be utilized for energy storage owed to fast proton transport rates. Lowering the scan rate allows more amount of time for the proton access the mass of the oxide [17].

3.2.4 Charge–discharge study:

The galvanostatic charge–discharge curves of the RuO_2 thin films were measured by chronopotentiometry technique between -1 V to +1 V at 5mA cm-2 in 0.1M KOH electrolyte. The charge-discharge curves Fig 6. shows a little iR drop when the sign of applied current is altered. After this ohmic response, the charge-discharge curves are approximately linear with charge and discharge time, which suggests that RuO_2 behaves as a capacitor. Hence, this material is a suitable electroactive material for supercapacitors. The energy density and efficiency decreased with increasing deposition coats. This result is analogous to that found for loading RuO_2 in a carbon electrode [18]. The highest energy efficiency of 83.33 %, specific power 36 KW/Kg and specific energy of 8.25 Wh/Kg was obtained for a film having 4 deposition coats.

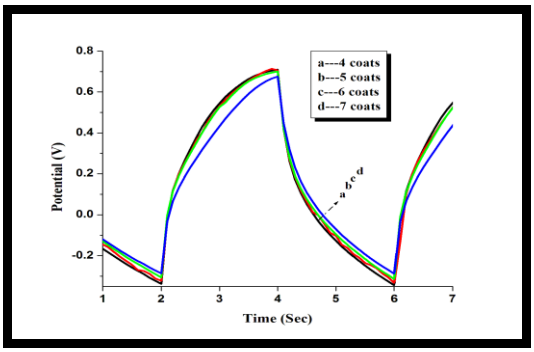

Fig 6. The charge–discharge curves of RuO_2 thin films measured at 5 mA/cm2 (a) 4 coats (b) 5 coats (c) 6 coats (d) 7 coats

3.2.5 Stability of electrode

The cyclic stability of RuO_2 electrode having 4 deposition coats in 0.1M KOH was investigated by continuous sweeping the potential for 1000 cycles between -0.55 - 0.55V at a scan rate of 200 mV/s. Fig. 7 shows the CV of 1st and 1000 th cycle.

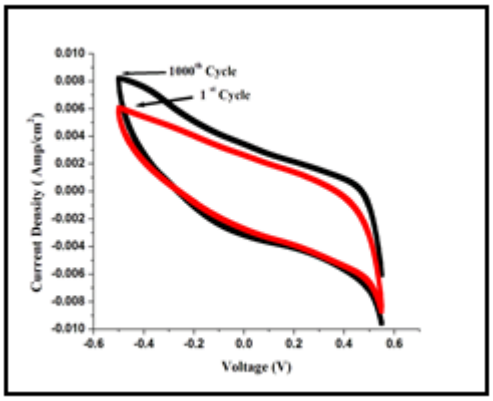

Fig 7. The CV curves of RuO_2 electrode at 1st and 1000th cycles for 200 mV/sec scan rate in 0.1 M KOH electrolyte for 4 deposition coats.

The current under curve is decreased by 17% up to 1000 cycles. We found that our system can resist about 1000 cycles with no a significant decrease in the capacity, illustrating a quite stable nature of RuO_2 electrode in energy storage application. The specific and interfacial capacitance values are decreased in small amount with the number of cycles due to the loss of active material. The capacitance decreased from 238 F/g to 196 F/g for 1000 th cycle as shown in figure 8.

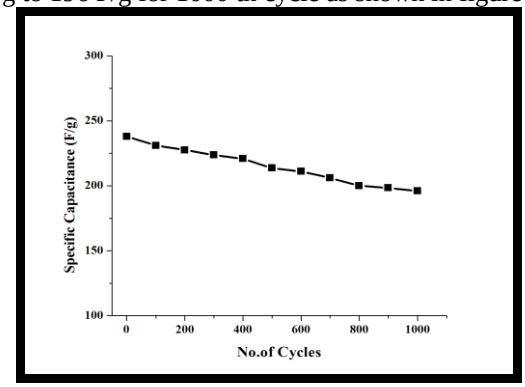

Fig 8. The specific capacitance variation with number of cycles for ruthenium oxide thin film having 4 deposition coats.

3.2.6 Electrochemical Impedance Spectroscopy

Fig. 9 shows the Nyquist plot for Ruthenium oxide thin film electrode having 4 deposition coats. EIS measurement was carried out at a dc bias of 0.083 V with a sinusoidal signal of 5 mV over the frequency range of 1 Hz to 10^5 Hz. A sharp increase in of the imaginary part of EIS at lower frequency is

due to capacitive behavior of the electrode. A semicircle at higher frequencies is due to the charge –transfer resistance. In the intermediate frequency region, the 45° line to Z' axis is the indication of ion diffusion into electrode materials. In the inset , the semicircle representing the charge transfer resistance at the electrode/ electrolyte is observed.

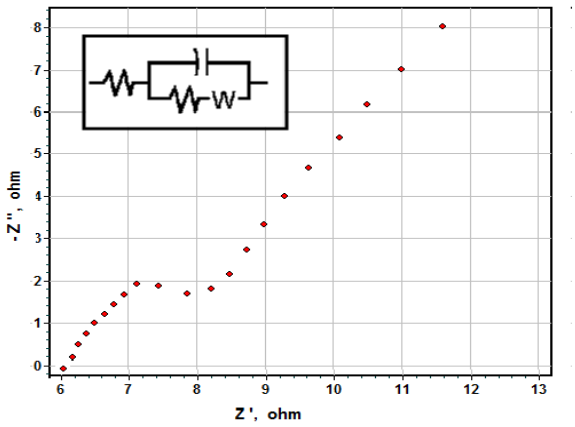

Fig 9. Impedance Spectroscopy (Nyquist Plot) of RuO_2 thin film for 4 deposition coats.

A simplified equivalent circuit is shown in an inset in above figure. C element represent double layer capacitance, R elements represent electrolyte resistance in pores, equivalent series resistance and Faradaic resistance and w is the Warburg diffusion resistance. The value of ESR estimated was 2.3 Ω. The lower ESR in the present case is attributed to the lower resistance of RuO_2 film which improves the redox activity during charging-discharging [19].Relatively low resistance is beneficial for high power [20].

4. Conclusions

From the above results, it is concluded that a sol-gel spin coated RuO_2 film can be used in the formation of supercapacitor. The highest value observed for the specific capacitance is 489 F /g for a RuO_2 film of 4 deposition coats. Even though the capacitance increases, the specific capacitance decreases with increasing film thickness. This is attributed to increase in crystallinity with increasing deposition coats. The highest energy density and power density of 8.25 Wh/Kg and 36 KW/Kg respectively was obtained for the same fim. The energy efficiency decreased with increasing film thickness. RuO_2 film can withstand about 1000 cycles without a significant decrease in the capacity, illustrating the fairly stable nature of RuO_2 electrode in energy storage application. The analysis of impedance spectra has been discussed to arrive at an equivalent circuit representing the ES. The sol-gel spin coating method is helpful for preparation of large area RuO_2 electrodes with amorphous structure for supercapacitive applications at the cost of small amount of preliminary ingredients.

5. Acknowledgements

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