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Morphological Study and Electrochemical properties of Ruthenium Oxide Thin Film

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ABSTRACT

There is a growing necessity of transition metal oxide thin film for many important technological applications such as smart windows gas sensors, solar cells, super capacitors etc. Among the other transition metal oxides, ruthenium oxide is a potential material as it exhibits interesting structural, optical, chemical, electrical properties. In this investigation ruthenium oxide thin films have been synthesized using spin coating technique. Here ruthenium oxide thin films have been deposited on stainless steel substrate by sol-gel spin coating method. Thin film properties of deposited samples were studied by XRD, SEM, FTIR, EDAX. AFM. The cyclic voltammetry study and chronopotentiometry was carried out with 0.1M KOH electrolyte to study the supercapacitor properties.

1. Introduction

Ruthenium oxide is superior due to the unique combination of characteristics, such as metallic conductivity, high chemical and thermal stability, catalytic activities, electrochemical redox properties, highly reactive with reducing agents due to its oxidizing properties and field emitting behaviour etc.[1]. It has been widely used in supercapacitor because of its good catalytic properties[2]. Ruthenium oxide thin films have been prepared using various techniques, including organometallic chemical vapour deposition[3], sol gel[4], electro deposition[5]. Here, attempts are made to deposit RuO2 thin films using sol-gel spin coating deposition technique. The structural ,morphological , vibrational properties were presented for as deposited films. The cyclic voltammetry study and chronopotentiometry was carried out with 0.1M KOH electrolyte to study the supercapacitor properties.

1.1 Experimental Deposition of RuO2 Thin Films

RuO2 thin films had been synthesized by a sol-gel spin coating technique using ruthenium trichloride as a source of Ruthenium oxide. In a typical experiment, 0.01 M solution of ruthenium trichloride was prepared. To obtain homogeneous solution a magnetic stirrer was used. After aging for 24 hours a gel was formed and then deposited on steel substrate by Spin coating unit. The sample was then rotated about 3000 rpm and films were annealed at a temperature of 900°C for 3 minutes. The deposition was repeated for number of time to increase the thickness of the film.

$$RuCl3.nH2O + (CH3)2CHOH \xrightarrow{900^0C} RuO2 + CH3CH2OH + HCL$$

2. Results and Discussions

A. Thin Film Characterization

1) Structural Characterization

The as deposited films were uniform, well adherent to the substrate and black in colour. Film crystallinity was analyzed using X-ray diffraction. The XRD patterns of RuO2 films on to the stainless steel substrate are shown in figure 1. The sharp intense peaks confirm the crystalline nature and tetragonal structure of the ruthenium oxide (JCPDS Card Number 65-2824) .These results are consistent with the results obtained by M. Khorasani-Motlagh, M. Noroozifar, M. Yousefi et.al.[6] The peaks having star mark corresponds to stainless steel. Table 1. gives the details of calculated and standard ‘d’ values and planes of RuO2 deposited thin films. The obtained values for the lattice parameters are a=b= 4.5200 A^o and c = 3.1272A^o which are in good agreement with the JCPDS data (65-2824).

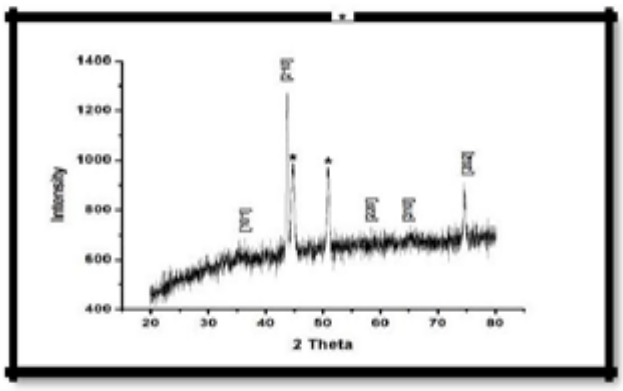

Fig 1. X-ray Diffractogram for RuO2 thin films on stainless steel substrate.

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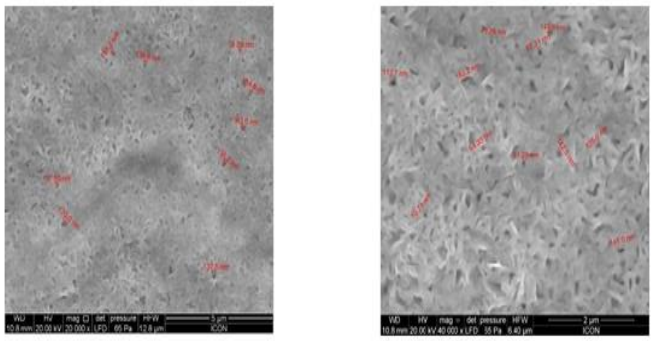
Table 1. Comparison of observed 'd' values, obtained from XRD data with the standard'd' values, from JCPDS card No-65-2824.

RuO2 (Films for this work)				RuO2 (Card No -65-2824)		
Peak No	2Θ	d	Intensity	d	Intensity	Plane
1	36.0323	2.5035	603	2.5654	715	[101]
2	44.8134	2.02084	985	2.0214	16	[210]
3	58.2545	1.5825	731	1.5980	11796	[220]
4	65.2598	1.4285	739	1.4293	96	[310]
5	73.5845	1.2861	727	1.2827	50	[202]

2) Surface Morphological Analysis

The surface morphological study of the RuO2 thin film has been carried out from SEM image. Figure 2 shows scanning electron microscopic (SEM) photographs of ruthenium oxide thin films at different magnifications. It showed that the substrate is well covered with RuO2 material. The SEM image shows non-uniformly distributed aggregates giving rise to a high surface roughness. The porous morphologies clearly found on these annealed RuO2 films which is favourable for penetration of electrolyte. In the inset, one can see the particles are well connected yet provide porous structure, which is much required for supercapacitors. The rough texture represents the grain boundary surfaces. The size of grains laid in the range 170 – 182.2 nm. In electrochemical supercapacitors, an increased amount of charge can be stored on the highly extended surface area created by large number of pores within a high surface area electrode material. Nano crystalline and porous materials as electrode material exhibit good electrochemical performance because these materials possess both a high surface area and pores which are adapted to the size of ions.



(a) (b)

Fig 2. SEM micrographs of RuO2 thin films at (a) (X20,000) and (b) (X40,000) magnifications.

3) EDAX analysis of RuO2 film

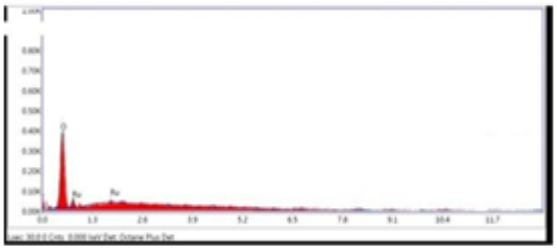


Fig 3.The energy dispersive X-ray (EDAX) analysis of RuO2 film.

Fig. 3 shows typical EDAX pattern of the RuO2 film The peaks for Ru and O were present in the spectrum confirming the formation of RuO2.The observed atomic percentages for Ru and O are shown in Table 4.1, which showed the RuO2 composite film is in non-stoichiometeric form.

Table 2. Elemental composition analyses of RuO2 film.

Element	Atomic %
O K	51.91
Ru	0.23

4) FTIR Spectroscopy

The FT-IR absorption spectrum of as-deposited RuO2 thin films in the range 4000–400 cm^{-1} is shown in fig. 3.4. From these spectra, it can be observed apparently that strong band Ru and O around at 759.70 cm^{-1}, 896.75 cm^{-1} are associated with the characteristic vibrational mode of rutile RuO2. This result indicated that, as deposited film contained hydroxide and other bonds, which indicates that formation of hydrous ruthenium oxide that may play important role in capacitive behavior

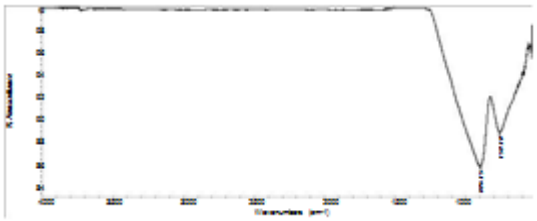


Fig 4. FT-IR spectrum of RuO2 deposited by spin coating method.

The infrared spectrum of as deposited RuO2 thin film depicts strong absorption bands at 759.70 cm^{-1}, 896.75 cm^{-1} indicating the stretching mode of Ru=O. The dominant band at 896.75$cm^{-1}$is associated with the vibration of Ru=O stretching [7-8] and band at 764 cm^{-1} indicates the weak O-Ru-O stretching. Bouzidi et al observed the similar results.[9]

5) AFM Study

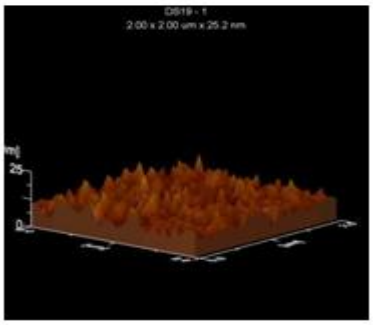


Fig 5.AFM image of sample Ru.

AFM scanning of the sample pure Ru was made to study the change in the surface morphology of the films (Fig.5). For measuring the surface roughness of the films, 2×2 m^2 surface area was utilized. The roughness of the sample is observed to be 25.2 nm.

B. Electrochemical Characterization

1) Cyclic Voltammetry Analysis

The electrochemical behaviour of RuO2 thin films was analyzed by cyclic voltammetry technique in 0.1 M KOH electrolyte. Cyclic voltammetry (CV) technique was used to investigate the supercapacitive properties of the RuO2, The CV curves of the RuO2 Fig. The CV curves of RuO2 were obtained in the potential window of 0 to +1 V vs SCE, as the area under the CV curves was observed maximum in this potential window for the respective electrode materials. The CV curves were carried out at 10 $mV.s^{-1}$ to 100mv, s^{-1} scan rate. The CV curve of RuO2 shows pseudocapacitive behavior in the potential window -1.5 to +1 V vs SCE. RuO2 electrode which is a distinct from that of the electric double-layer capacitance. The appearance of single pair of redox peaks indicates that the RuO2 gives rise to pseudocapacitance of the electrode. At lowest scan rate 10 $mV.s^{-1}$, maximum specific capacitance is found to be 1010 $F.g^{-1}$. The decreasing trend of the capacitance suggests that parts of the surface of the electrode material are inaccessible at high charging–discharging rates. Hence, the specific capacitance obtained at the slow scan rates is believed to be closest to that of full utilization of the electrode material. At lowest scan rate of 10 $mV.s^{-1}$, maximum specific capacitance is found to be 1010$F.g^{-1}$. The capacitive behaviour of the oxide is enhanced by rectangular shape of the plot. [12]

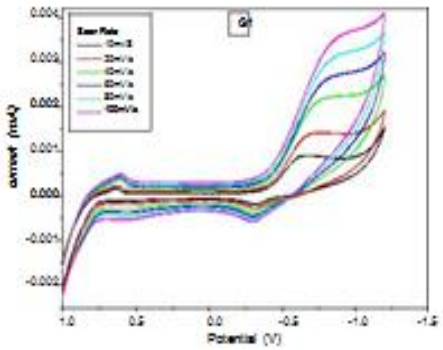


Fig 6. CV of RuO2 with different scan rate.

Fig. 7 shows the variation of specific and interfacial capacitance with scan rate. The decreasing trendof the capacitance suggests that parts of the surface of the electrode material are inaccessible at high charging–discharging rates. Hence, the specific capacitance obtained at the slow scan rates is believed to be closest to that of full utilization of the electrode material. Fig. shows the variation of interfacial capacitance with scan rate of the RuO2 thin films. It is observed that the as scan rate increases the interficical capacitance decreases. Similar inclinations were reported in the literature [13].

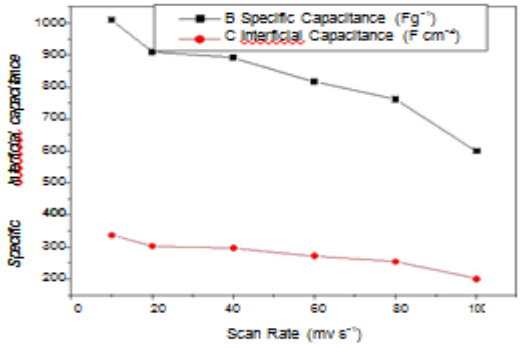


Fig 7. Variation of specific and interficial capacitance with scan rate.

2) Galvanostatic Charge –Discharge Analysis

The charge–discharge behaviour of the RuO2 thin films was examined by chronopotentiometry in the potential range of - 0.7 to + 0.7 V vs. SCE at 2 $mA.cm^{-2}$ current density. The charge-discharge curves of RuO2 thin films are shown in Fig. The charge-discharge curve of RuO2 shows the approximately linear charge and discharge time, The supercapacitor parameters such as specific power (SP), specific energy (SE) and columbic efficiency (η) are calculated are shown in Table 3.

Table3. Supercapacitive parameters of RuO2 thin film electrodes.

Parameters/ Material ↓	RuO2 →
Specific Power (S.P.) $kWhkg^{-1}$	28.706
Specific Energy (S.E.) $Wh.kg^{-1}$	7.9101
Columbic Efficiency (η) %	99.30%

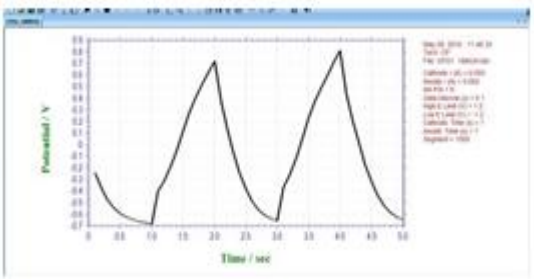


Fig 8. Galvanostatic charge-discharge curves of RuO2.

3) Stability Study RuO2 thin films

The stability and reversibility of an electrode material are important for its use in an electrochemical supercapacitor. Stability of RuO2 composite electrode was tested by cyclic voltammetry. Fig. 4.15 shows the CV curves of RuO2 electrode at the scan rate of 100 mV.s-1 within the voltage range - 1.2 to + 1.0 V vs. SCE for 1st and 1000th number of cycle. The current under curve is decreased by 11 % up to 1000 cycles. We found that our system can withstand about 1000th cycles without a significant decrease in the supercapacity, illustrating the fairly stable (89%) nature of RuO2 electrode in energy storage application. The specific and interfacial capacitance values are decreased by small amount with the number of cycles due to the loss of active material

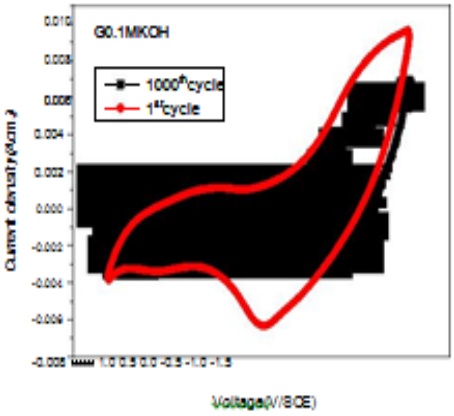


Fig 9. The CV curves of RuO2 thin film electrode at 1st and 1,000th cycles.

Fig. shows stability study of RuO2 thin films. Figure shows the 79% stability of RuO2 over the 1000th cycles.

It is observed that the material showed the excellent stability over the 1000^{th} cycles.

3. Conclusions

In conclusion, RuO2 thin films were deposited on stainless steel substrate by sol-gel spin coating method. The suitable annealing temperature was 900°C.The structural study showed the rutile structure of ruthenium oxide. The SEM images showed the pores morphologies and rough surfaces. IR spectroscopy showed the structure transformations of RuO2 phases. C-V plot showed the rectangular shape and maximum specific capacitance $1010F.g^{-1}$at a scan rate of 10 $mVSec^{-1}$. The Specific Power, Specific Energy and Columbic Efficiency of the RuO2 thin film electrode were calculated based on the charge/discharge curves are 28.706 $kWhkg^{-1}$, 7.9101 $Wh.kg^{-1}$ and 99.30% respectively. A stability of RuO2 is 79%. The specific and interfacial capacitance values are decreased in small amount with the number of cycles due to the loss of active material.

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