iJRASET
International Journal For Research in Applied Science and Engineering Technology

INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Volume: 4 **Issue:** VIII **Month of publication:** August 2016

DOI:

www.ijraset.com

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Volume 4 Issue VIII, August 2016
ISSN: 2321-9653
International Journal for Research in Applied Science & Engineering Technology (IJRASET)

Ruthenium Oxide: Thin Film and Electrochemical Properties

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Abstract: ***Electrochemical supercapacitors have attracted increased interest due to their high power density and long life cycle compared to batteries and high energy density compared to conventional capacitors. In recent years various metal oxides have involved attention for use as electrochemical capacitors in high power applications. In particular Ruthenium Oxide offer the advantage of providing higher energy density and electrochemical stability compared to carbon and polymer materials. 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. Thin films were used as electrodes for supercapacitor with 0.1 M KOH electrolyte. It showed maximum capacitance of 581 F/g for 4 coats at spin rate of 5 mv/sec. Also stability of the electrode was calculated. Power density and energy density were determined from galvanostatic charge-discharge analysis.***
Keywords: Supercapacitor, Ruthenium oxide, Sol-gel Spin-coating, CV, Galvanostatic charge-discharge

I. INTRODUCTION

Supercapacitors are the best candidates to provide the high power and long durability needed for the new energy devices [1]. The high capacity of supercapacitors mainly comes from the faradaic reaction within electroactive materials [2] The performance of Supercapacitor is attributed to the high electrochemical reversibility of redox transitions within electrode materials.[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] Among 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 ,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.

II. EXPERIMENTAL

The ruthenium oxide 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 different temperatures so as to get the better results needed for supercapacitor application .The film formation is explained in detail elsewhere.[9]

A. Optimization of Temperature

Thin films of Ruthenium oxide were prepared by sol-gel spin coating technique. The films used here were of 4 deposition coats. A suitable annealing temperature was determined by the study of structural analysis (XRD) . The thin films were annealed at 200°C, 400°C, 600°C, 800°C and 900°C.The change in structural behaviour at every change in temperature was observed.

III. RESULTS AND DISCUSSION

A. Thin Film Characterization

1) Structural Analysis: Figure1 shows the XRD pattern for ruthenium oxide thin films annealed at different temperatures. At lower temperature dominant peaks were not observed. The broad peaks observed at lower temperatures indicate the RuO_2 present is amorphous. As the temperature was increased the dominating peaks corresponding ruthenium were observed. Literature survey

Volume 4 Issue VIII, August 2016
ISSN: 2321-9653
International Journal for Research in Applied Science & Engineering Technology (IJRASET)

shows that transition from amorphous to crystalline RuO_2 occurs at high temperature and at 900°C the crystalline phase is observed.[10-11]

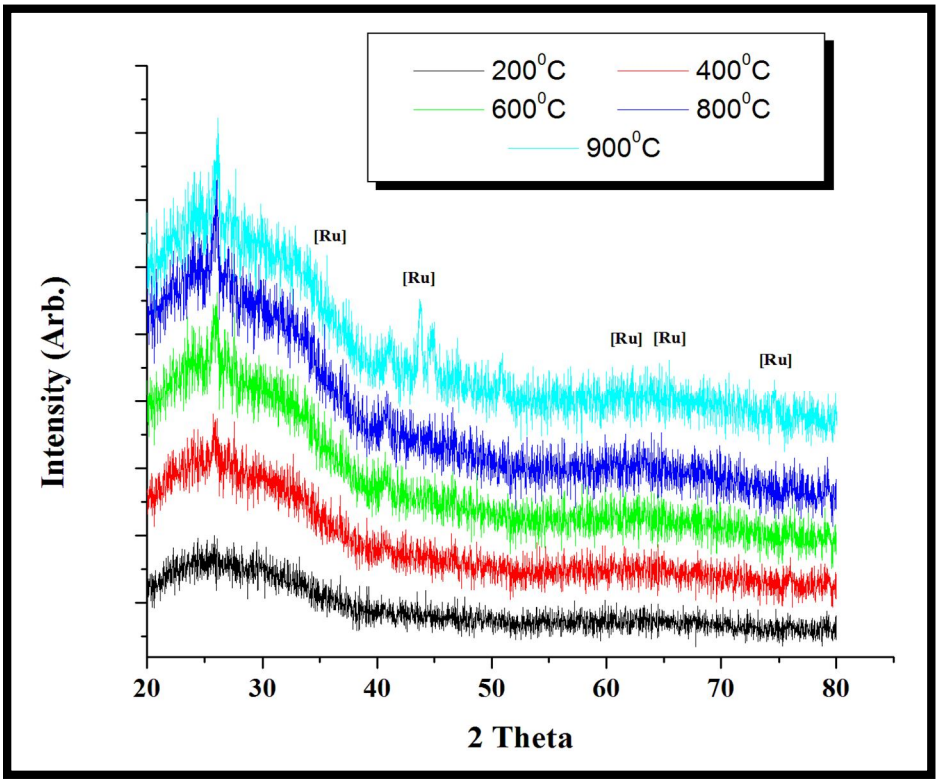

Figure 1.XRD pattern for ruthenium oxide thin films annealed at different temperatures.

It is observed from literature survey that synthesis temperatures of greater than or equal to 500 °C support the formation of crystalline RuO_2 phases.[12] Though the peaks of RuO_2 were observed for 800°C , they were not so dominant .Figure 2.shows the XRD pattern for RuO_2 thin film annealed at 900°C.

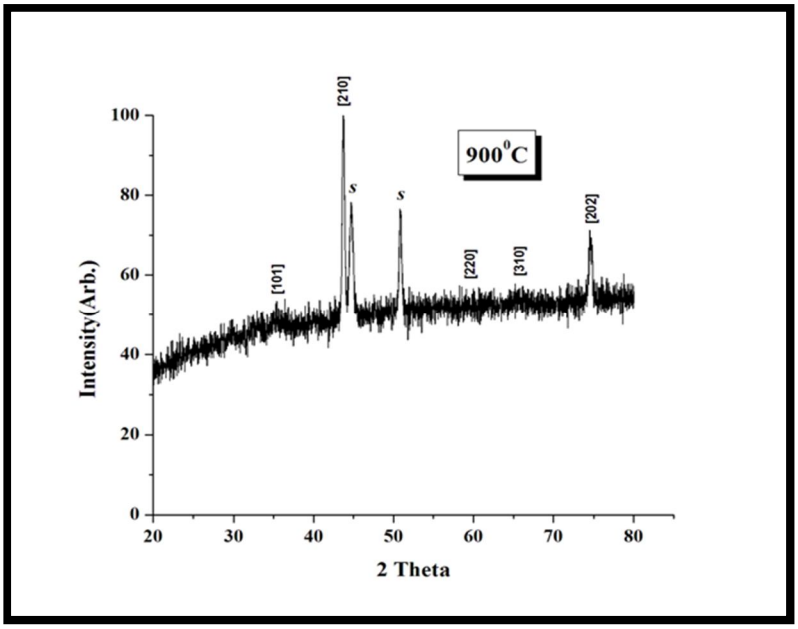

Figure 2. XRD pattern for RuO2 thin film annealed at 900°C.

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XRD pattern shows the dominating peaks at 35.1°, 44°, 60°, 66° and 75° corresponding to [101],[210],[220],[310] and[202] planes respectively confirming the crystalline formation of ruthenium oxide. Crystalline nature and tetragonal structure of ruthenium oxide was confirmed by sharp intense peaks (JCPDS Card Number 65-2824 and 88-0322). The details of structural analysis are published elsewhere[13].

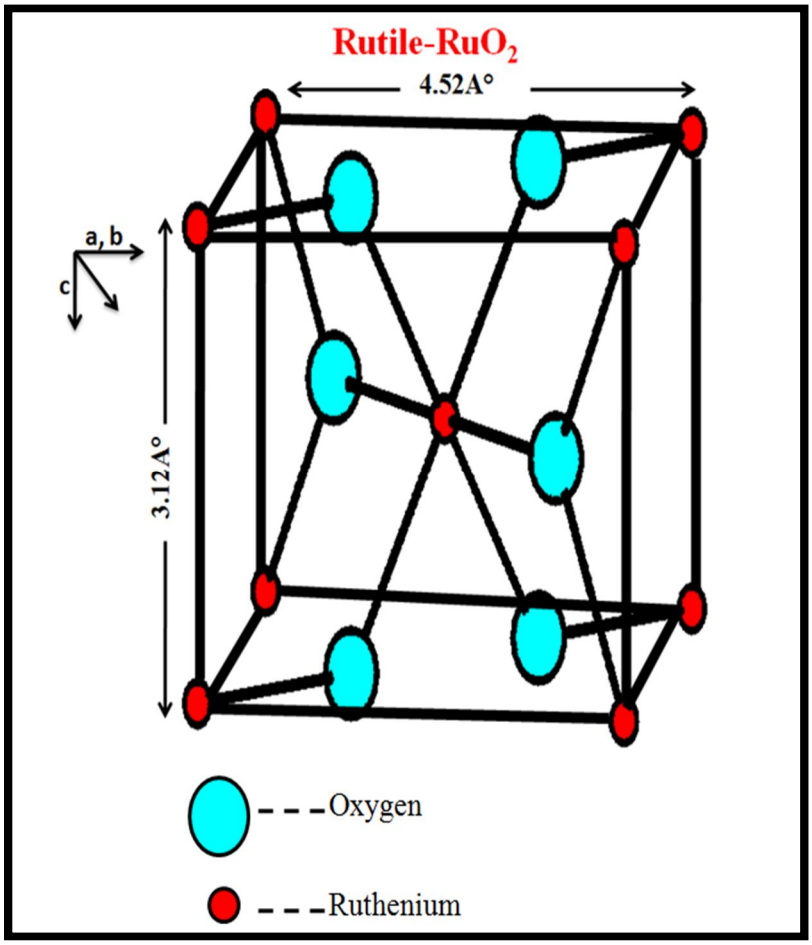

Figure 3. Rutile Structure of Ruthenium Oxide

RuO_2 adopts the rutile structure. Rutile has a body-centred tetragonal unit cell, with unit cell parameters a=b=4.52 A°, and c =3.12 A°. The ruthenium cations have a coordination number of 6 meaning they are surrounded by an octahedron of six oxygen atoms. The oxygen anions have a co-ordination number of three resulting in a trigonal planar co-ordination. Figure 3.shows the rutile structure of ruthenium oxide.

2) *Surface Morphological Analysis:* The surface morphological study of the RuO_2 thin film has been carried out from SEM image. Figure 4. shows scanning electron microscopic (SEM) photographs of ruthenium oxide thin films at different magnifications. It showed that the substrate is well covered with RuO_2 material. The SEM image shows non-uniformly distributed aggregates giving rise to a high surface roughness. The porous and "mud-cracked" morphologies clearly found on these annealed RuO_2 films which is favourable for penetration of electrolyte. The large cracks are attributed to the presence of inner stress in forming a crystalline RuO_2 film during the high temperature preparation step. 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 pores laid in the range 40-50 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. Nanocrystalline 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. [14-16]

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International Journal for Research in Applied Science & Engineering Technology (IJRASET)

(a) (b)

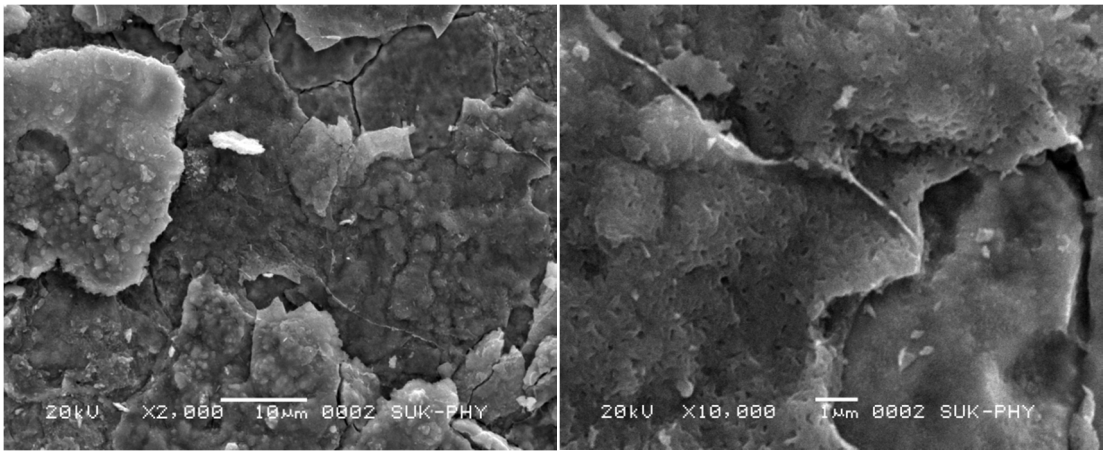

Figure 4. SEM images of ruthenium oxide thin films (a) X2000 (b) X10000 magnification.

The compositional analysis of the as deposited RuO_2 thin film was carried out using EDAX technique by Quanta 200 ESEM instrument. The typical EDAX pattern given in figure 5. shows the formation of RuO_2 on the substrate.

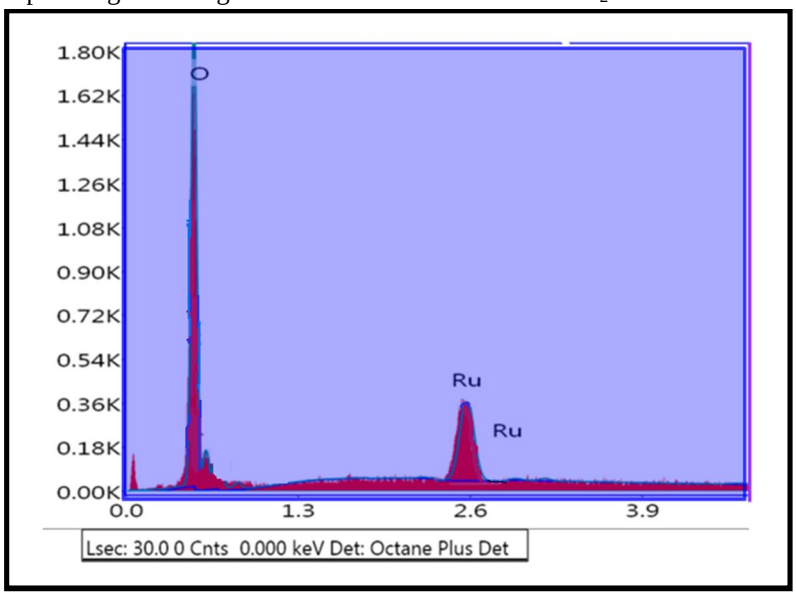

Figure 5. EDAX pattern of RuO_2 thin film.

3) *FTIR Spectroscopy:* For study of surface features of materials and for the examination of absorbed molecules on a solid surface, Fourier Transform infrared spectroscopy is a well known technique.IR spectroscopy was used to obtain additional information on the phases as well as structure transformations of RuO_2 phases. Figure 6. describes the dependence of optical spectra in the range 500 to 4000 cm^{-1} for Ruthenium Oxide thin films. The infrared spectrum of as deposited RuO2 thin film depicts strong absorption bands I and II at 880.41cm^{-1} and 749.52 cm^{-1} respectively indicating the stretching mode of Ru=O. The dominant band at 880.41 cm^{-1} is associated with the vibration of Ru=O stretching. [17-18] and band at 749.52 cm^{-1} indicates the weak O-Ru-O stretching. Bouzidi et al observed the similar results.[19]

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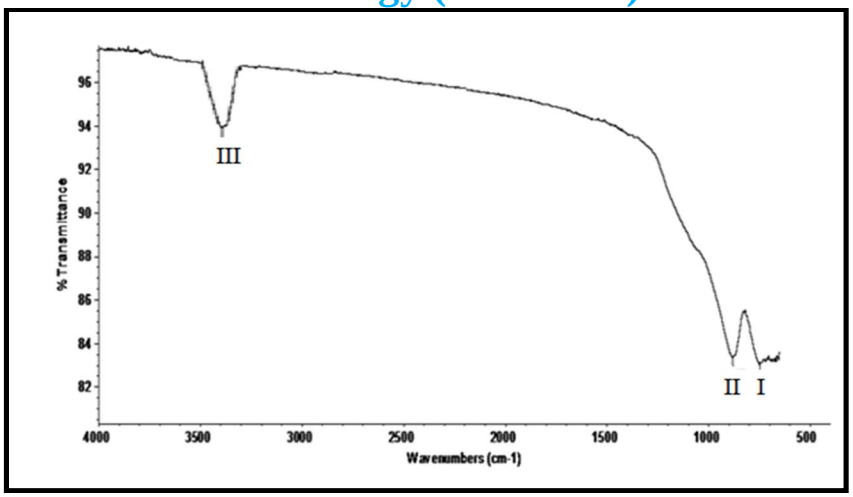

Figure 6. FTIR Spectrum of RuO_2 Thin Films.

The absorption band at III that is 3410 cm^{-1} is attributed to the stretching vibration stretching vibrations of OH^-. 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 [20]

B. Electrochemical Characterization

1) Cyclic Voltammetry Analysis: The electrochemical behaviour of RuO_2 thin films was analyzed by cyclic voltammetry technique in 0.1 M KOH electrolyte. Figure7. shows the C-V of ruthenium oxide thin film electrodes annealed at 900°C temperature. The capacitive behaviour of the oxide is enhanced by rectangular shape of the plot. [21] The electrode potential scanned between -600 mV to 800 mV in both anodic and cathodic directions for a thin film electrode annealed at 900°C showed the typical pseudocapacitive behaviour.

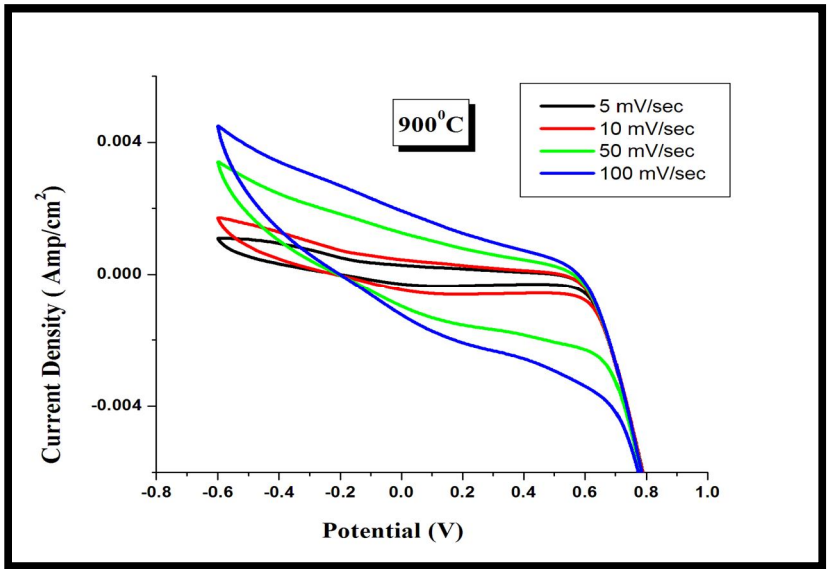

Figure 7. Cyclic voltammogram of Ruthenium oxide thin films annealed at (a) 200°C(b) 400°C(c) 600°C(d) 800°C and (e) 900°C

The specific capacitance decreased with increase in current density. The decrease in specific capacitance with increase in current density is attributed to decrease in the efficiency of material utilization of the active material at high current densities. Similar inclination were reported in the literature[22].When the scan rate is low, interaction of the active material with the inner surface increases and when the scan rate is high, surface of electrode material that is accessible is less. That shows the increase in CV plot area and decrease in specific capacitance. Full utilization of electrode material is believed to be at lower scan rates. It showed

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maximum specific capacitance of 581 F/g at a scan rate of 5 mV/Sec.

2) Galvanostatic Charge –Discharge Analysis: The galvanostatic charge–discharge curves of the RuO_2 thin films were measured by chronopotentiometry technique between -1 V to +1 V in 0.1M KOH electrolyte.

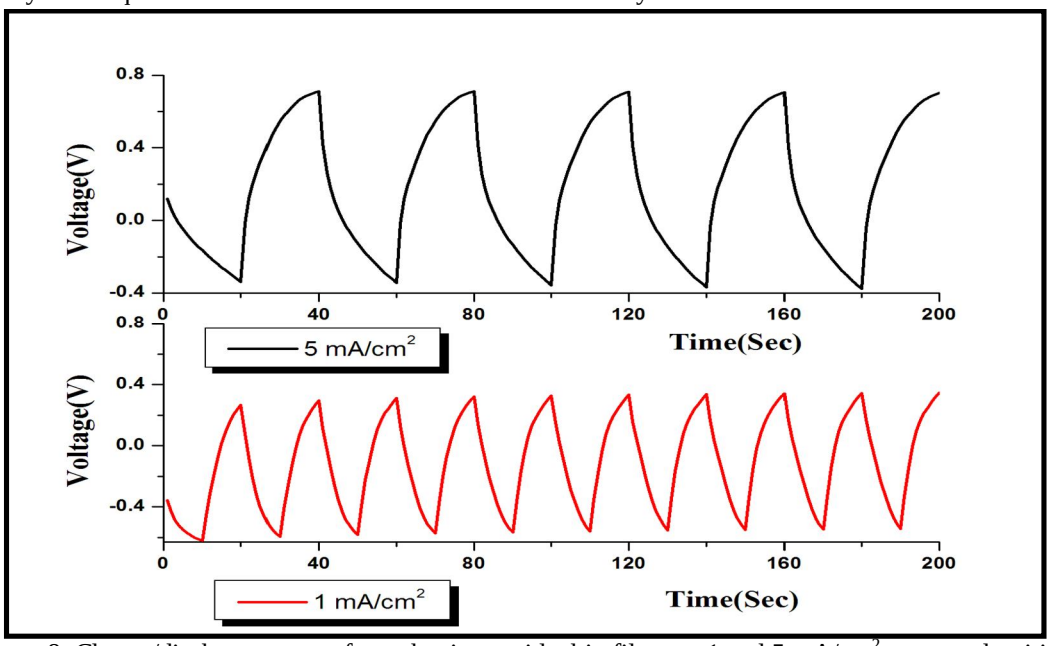

Figure 8: Charge/discharge curves for ruthenium oxide thin films at 1 and 5 mA/cm^2 current densities.

The galvanostatic charge/ discharge curves of ruthenium oxide thin film electrode at different current densities as 1, 2,3,4,5,mA/cm^2 was studied but for the current densities 1 mA/cm^2 and 5 mA/cm^2 are shown in figure 8. A typical capacitive behaviour was indicated by the linear relationship between voltage and time. The interfacial capacitances of the RuO_2 thin film electrode were calculated based on the charge/discharge curves. The highest areal capacitance of the RuO2 electrode can reach about 48 mF/cm^2 at a current density of 1 mA/cm^2 which is larger than the values reported for other composite electrodes, such as SnO_2:RuO_2 (35mF cm^2) and PANI-RuO_2 composite(7 mF/cm^2) [23] Even at a high current density of 5 mA/cm2, RuO2 electrode can still deliver a high areal capacitance of 40 mF/cm^2, which indicates better rate performance. Figure 9.shows the variation of interfacial capacitance with current density.RuO_2 thin film electrode showed the energy density of 36 KW/kg and power density of 8 Wh/Kg.

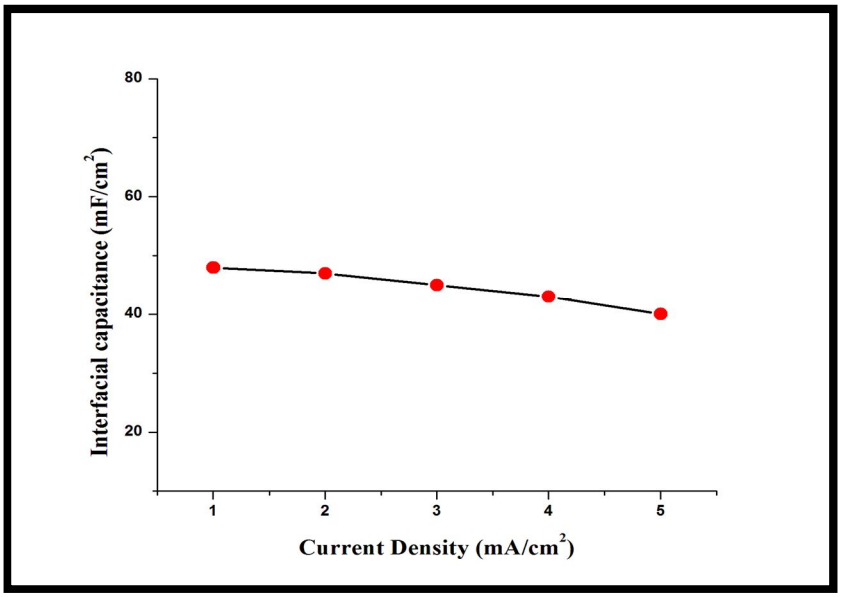

Figure 9. The Interfacial capacitance of the Ruthenium oxide thin film at different current densities.

3) *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 as shown in figure 10. The current under curve is decreased by 17% up to 1000 cycles. 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. The initial high value of the capacitance may be due to the electrode activation process, involving the penetration of the electrolyte into the electrode , resulting in an increase of the electrode–electrolyte interface. The decrease of the capacitance for the following cycles is probably due to the dissolution or loss of the active material into the electrolyte during the long time cycling. No capacitance loss was achieved by the film after 1000 cycles, signifying better cycling stability of the ruthenium oxide thin film electrode.

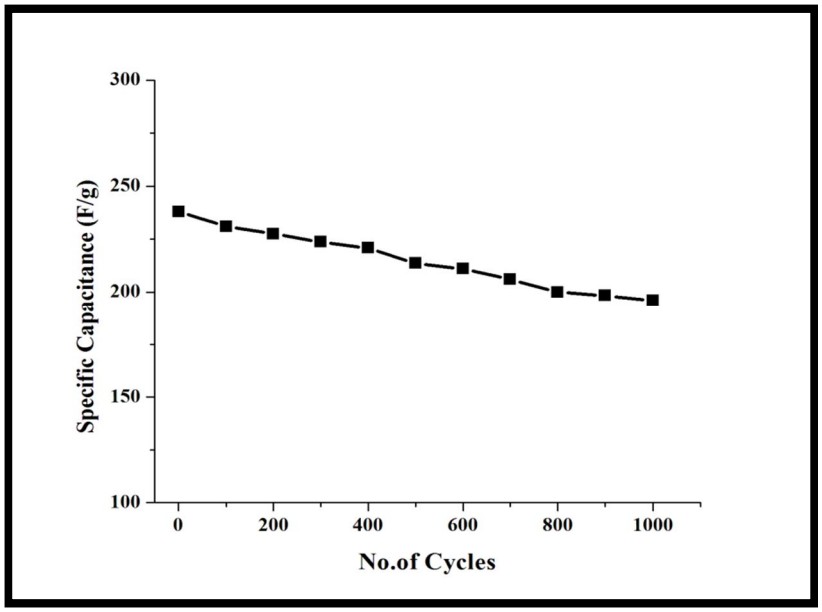

Fig 10. The specific capacitance variation with number of cycles for Ruthenium oxide thin film having 4 deposition coats.

IV. CONCLUSIONS

In conclusion, RuO_2 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 mud-cracked morphologies with random and rough surfaces. IR spectroscopy showed the structure transformations of RuO_2 phases. C-V plot showed the rectangular shape and maximum specific capacitance 581 F/g at a scan rate of 5 mV/Sec. The interfacial capacitances of the RuO_2 thin film electrode were calculated based on the charge/discharge curves. A typical capacitive behaviour was indicated by the linear relationship between voltage and time The highest areal capacitance of the RuO_2 electrode can reach about
48 mF/cm^2 at a current density of 1 mA/cm^2 . The specific and interfacial capacitance values are decreased in small amount with the number of cycles due to the loss of active material.

V. ACKNOWLEDGEMENT

The Authors wish to acknowledge the U.G.C, New Delhi for financial support through the Major Research Project F No. 42-123/2013(SR).

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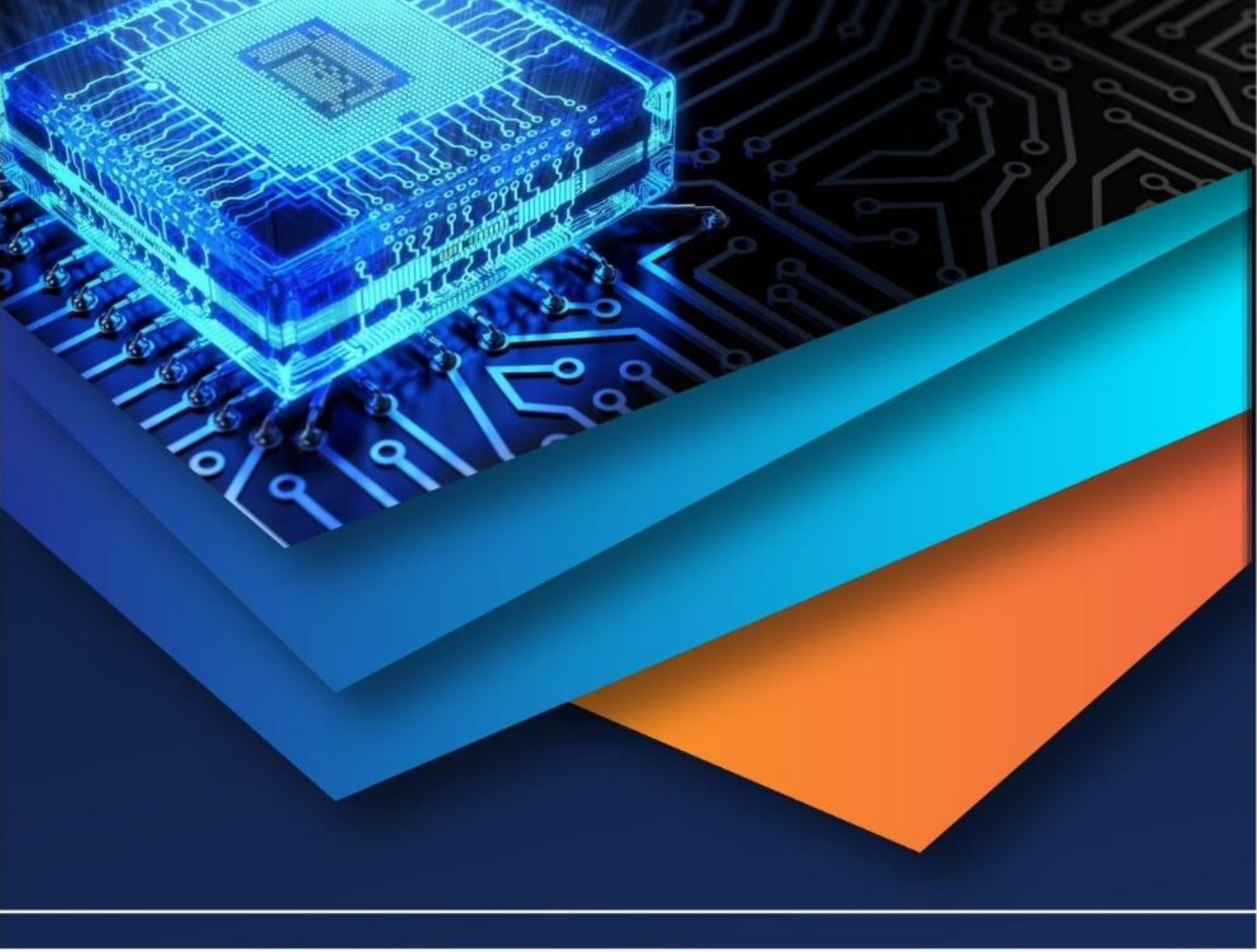

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