### CHAPTER-III

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### SECTION B

**SUPERCAPACITIVE PERFORMANCE OF TIN OXIDE RUTHENIUM OXIDE COMPOSITE THIN FILMS**

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SECTION A: SYNTHESIS AND CHARACTERIZATION OF TIN OXIDE RUTHENIUM OXIDE COMPOSITE THIN FILMS BY SUCCESSIVE IONIC LAYER ADSORPTION AND REACTION (SILAR) METHOD

3.A.1 Introduction

There are various methods used in the literature to deposit tin oxide-ruthenium oxide (SnO$_2$-RuO$_2$) composite in powder and/or in thin film form such as sol-gel, hydrothermal and sputtering [1-3]. In case of sol-gel method, the steps involved for preparation of composite are very complicated and not easily controllable. The final product in sol-gel and hydrothermal method is in powder form, which undergoes through various processing steps to prepare the electrode for studying the supercapacitive properties. On the other hand, sputtering method for deposition of composite film is not cost effective, as it requires sophisticated instrumentation. Therefore, there is a need to use a simple and inexpensive method that directly yields composite in thin film form. One such method is successive ionic layer adsorption and reaction (SILAR) method.

The present chapter is divided into two sections, section A deals with the synthesis and characterization of SnO$_2$-RuO$_2$ composite films by SILAR method and section B deals with their supercapacitive performance.

3.A.2 Experimental Details

3.A.2.1 Substrate Cleaning

Substrate cleaning plays an important role in the deposition of thin films. Extreme cleanliness of the substrate is required for the deposition as the contaminated substrate surface provides nucleation sites facilitating growth resulting non-uniform films. Stainless steel is used as substrate because to study the supercapacitive properties, conducting substrate is necessary requirement. Stainless steel substrates were cleaned according to the following procedure.
1. The substrates were mirror polished using zero grade polish paper,
2. The substrates were washed with detergent and double distilled water,
3. Then, the substrates were ultrasonically cleaned for 15 min, and
4. Finally, the substrate were dried by air and used for the deposition.

3.A.2.2 Solution Preparation

In the present work, stannous chloride (Sn(II)Cl₂.2H₂O) and ruthenium chloride (Ru(III)Cl₃.xH₂O) solutions are prepared in double distilled water as sources of Sn⁴⁺ and Ru³⁺ ions, respectively for the deposition of SnO₂-RuO₂ composite films.

3.A.2.3 Experimental Setup for the Deposition of Tin oxide Ruthenium oxide (SnO₂-RuO₂) Composite Thin Films by SILAR Method

The SnO₂-RuO₂ composite thin films were deposited on stainless substrates by SILAR using 5-beakers system. The schematic experimental setup for deposition is shown in Fig. 3.1. The cationic solutions of 0.05 M stannous chloride (SnCl₂.2H₂O) and 0.01 M ruthenium chloride (RuCl₃.xH₂O) are taken in separate beakers as sources of tin (Sn⁴⁺) and ruthenium (Ru³⁺) ions respectively. The anionic solutions consist of separate solutions of 1% H₂O₂ and hot water maintained at 343 K as sources of oxygen and OH⁻ ions respectively.

3.A.2.4 Deposition of SnO₂-RuO₂ Composite Thin Films by SILAR Method

The deposition of SnO₂-RuO₂ composite thin films were carried out on stainless steel substrates using SILAR method. In this method, substrates were immersed alternatively in the separately placed ion carrying precursor solutions with regular intervals.

The deposition of SnO₂-RuO₂ thin film by SILAR method consists of five steps as follows;
a) In the first step, pre-cleaned stainless steel substrate is immersed in stannous (Sn^{4+}) chloride solution placed in beaker 1 (Fig. 3.1) so as the stannic species are adsorbed on the substrate surface. The adsorption time is optimized to 20 s.

b) In the second step, the substrate with stannic species on the surface is immersed in beaker 2 (Fig. 3.1) containing dilute H_{2}O_{2} solution for 40 s. The stannic species react with H_{2}O_{2} to form SnO_{2}.

c) The substrate with SnO_{2} on its surface is rinsed in double distilled water kept in beaker 3 (Fig. 3.1) for 20 s to remove the excess H_{2}O_{2} and loosely adsorbed SnO_{2} particles.

d) The substrate coated with SnO_{2} is immersed in beaker 4 (Fig. 3.1) containing RuCl_{3} solution to adsorb the Ru^{3+} ions, the adsorption time is optimized to 20 s.

e) In this case, the substrate with pre adsorbed Ru^{3+} ions is then immersed in beaker 5 (Fig. 3.1) containing hot water (343 K) for 40 s so the reaction occurs between Ru^{3+} ions and OH^{-} ions tends to form RuO_{2}.

These five steps consist one cycle for formation of SnO_{2}-RuO_{2} composite film. In order to vary the content of SnO_{2} and RuO_{2} in the composite films, the cycle ratio of SnO_{2}:RuO_{2} deposition is varied. For e.g. in the preparation of SnO_{2}:RuO_{2} composite having cycle ratio 3:2, the steps a) to c) for deposition of SnO_{2} are repeated for three times and then the steps d) to e) for RuO_{2} deposition are repeated for two times. This consists of a single step for the formation of SnO_{2}-RuO_{2} composite film having SnO_{2}:RuO_{2} cycle ratio 3:2. Similar procedure is followed for the preparation of composite films of SnO_{2}:RuO_{2} cycle ratio as 1:1, 1:3 and 2:3. The SnO_{2}-RuO_{2} composite films of 3:2, 1:1, 1:3 and 2:3 cycle ratios are named as S1, S2, S3 and S4, and used in further studies.
Fig. 3.1: Schematic experimental setup of SILAR method for deposition of SnO₂-RuO₂ composite film.

3.A.2.5 Characterization Techniques

The thickness of SnO₂-RuO₂ composite films was measured by weight difference method using a sensitive microbalance. The structure of SnO₂-RuO₂ thin films identified by X-ray diffraction analysis were performed on a Philips (PW 3710) diffractometer with chromium target (λ = 2.28 Å). The FT-Raman spectrograms were obtained using Bruker make Raman spectrophotometer. The FT-IR spectra of the samples were collected using a ‘Perkin Elmer, FT-IR Spectrum one’ unit. The surface morphology and compositional studies of films were carried out using scanning electron microscopy (FESEM- JSM 7100 F) attached with an energy-dispersive X-ray analysis (EDAX) analyzer to measure the sample composition. Static water contact angle measurement was carried out using Rame-Hart
Instrument Co., USA equipped with CCD camera. The supercapacitor studies were carried out using the 263A EG & G Princeton Applied Research Potentiostat forming an electrochemical cell comprising SnO$_2$-RuO$_2$ composite film as a working electrode, platinum as a counter electrode and saturated calomel electrode (SCE) as a reference electrode. The charge-discharge study was performed by WonATech Automatic Battery Cycler WBCS system, interfaced to a computer. The electrochemical impedance measurements were conducted with a versastat 3G frequency response analyzer (FRA) under Zplot program (Scribner Associates Inc.)

3.A.3 Results and Discussion

3.A.3.1 Reaction Mechanism of SnO$_2$-RuO$_2$ Composite Thin Film Formation

The general reaction mechanism for SnO$_2$-RuO$_2$ composite film formation by SILAR can be described as follows. First 0.05 M SnCl$_2$,2H$_2$O was dissolved in concentrated hydrochloric acid and the mixture was kept for heating at 363 K for 5 min. The reaction proceeds as,

$$\text{SnCl}_2 \cdot 2\text{H}_2\text{O} + 2\text{HCl} \xrightarrow{\Delta} \text{SnCl}_4 + 2\text{H}_2\text{O} + 2\text{H}^+$$  \hspace{1cm} (3.1)

In aqueous acidic solution, Sn$^{4+}$ ions hydrolyze to form highly insoluble stannic hydroxide (Sn(OH)$_4$) which precipitates on the substrate surface immersed in it.

$$\text{Sn}^{4+} + 4\text{H}_2\text{O} \rightarrow \text{Sn(OH)}_4 + 4\text{H}^+$$ \hspace{1cm} (3.2)

The substrate covered with Sn(OH)$_4$ is rinsed in dilute H$_2$O$_2$ solution, where the formation of SnO$_2$ takes place as,

$$\text{Sn(OH)}_4 + \text{H}_2\text{O}_2 \rightarrow \text{SnO}_2 + 3\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \uparrow$$ \hspace{1cm} (3.3)

The substrate coated with SnO$_2$ is then rinsed in double distilled water in order to remove loosely bound particles and excess H$_2$O$_2$ from the substrate surface. It is observed that if this step was not followed, then
excess H$_2$O$_2$ on the substrate surface reacts with RuCl$_3$ solution and precipitation of ruthenium hydroxide (Ru(OH)$_3$) is observed in RuCl$_3$ solution without RuO$_2$ film formation. To avoid this, it is necessary to rinse the substrate in double distilled water after SnO$_2$ film formation.

The mechanism for RuO$_2$ film formation is same as described by Patake and Lokhande [4]. The substrate coated with SnO$_2$ is immersed in RuCl$_3$ solution, where the Ru$^{3+}$ ions are adsorbed on the substrate surface. The substrate with adsorbed Ru$^{3+}$ ions is immersed in hot water bath (343 K) where OH$^-$ ions react with Ru$^{3+}$ ions to form Ru(OH)$_3$ through the reaction,

$$\text{Ru}^{3+} + 3\text{OH}^- \rightarrow \text{Ru(OH)}_3 \quad (3.4)$$

The excess OH$^-$ ions then react with Ru(OH)$_3$ to form RuO$_2$ as,

$$\text{Ru(OH)}_3 + \text{OH}^- \rightarrow \text{RuO}_2 + 2\text{H}_2\text{O} \quad (3.5)$$

This completes the one cycle for SnO$_2$-RuO$_2$ composite film formation. The composite films of various cycle ratios are prepared by keeping total number of cycles constant.

### 3.A.3.2 Thickness Measurement

The thickness of the films was measured in terms of weight deposited per unit area due to the porous morphology of the film [5]. The total number of cycles was kept constant at 35 for all the cycle ratios. Fig. 3.2 shows the photograph of SnO$_2$-RuO$_2$ composite films for various cycle ratios on stainless steel substrate (> 8 cm$^2$ area) proving the feasibility of SILAR method for large area deposition. The composite films with higher number of cycles for SnO$_2$ deposition are gray colored, which changes to black for increased RuO$_2$ cycles. The composite films are uniform and well adherent to the substrate surface. Fig. 3.3 shows the variation of thickness of composite film with cycle ratios. The different thickness observed for samples S1, S2, S3 and S4 may be due to the different growth kinetics of SnO$_2$ and RuO$_2$ formation.
CHAPTER III: SYNTHESIS AND CHARACTERIZATION OF TIN OXIDE RUTHENIUM OXIDE COMPOSITE THIN FILMS BY SUCCESSIVE IONIC LAYER ADSORPTION AND REACTION (SILAR) METHOD AND THEIR SUPERCAPACITIVE PERFORMANCE

Fig. 3.2 Photograph of SnO$_2$-RuO$_2$ composite films deposited by SILAR on stainless steel substrate (>8 cm$^2$ area)

Fig. 3.3: Variation of film thickness of SnO$_2$-RuO$_2$ composite thin films with cycle ratio.
3.4.3.3 Structural Studies

The X-ray diffraction patterns of SnO$_2$-RuO$_2$ composite films with various cycle ratios are presented in Fig. 3.4. For the S1 sample, broad diffraction peaks are observed at the $2\theta=39.06^0$ and $50.92^0$ which correspond to the (1 1 0) and (1 0 1) planes of cassiterite SnO$_2$, respectively (JCPDS card no.77-0452). No diffraction peaks for RuO$_2$ are observed which might be due the formation of amorphous RuO$_2$ in composite. The formation of amorphous RuO$_2$ was observed in the low temperature chemical synthesis [4, 6]. The sample S2, showed the broader diffraction at the above angles as compared with sample S1 which revealed the formation of oxide in nanometer scale. In case of samples, S3 and S4, no broader diffractions are observed (fig. 3.4 c and d) which may be due to the increased RuO$_2$ content in the film. The diffraction peaks observed in these two samples correspond to the transition from nanocrystalline to amorphous phase of composite films with increase in RuO$_2$ content in the composite.
CHAPTER III: SYNTHESIS AND CHARACTERIZATION OF TIN OXIDE RUTHENIUM OXIDE COMPOSITE THIN FILMS BY SUCCESSIVE IONIC LAYER ADSORPTION AND REACTION (SILAR) METHOD AND THEIR SUPERCAPACITIVE PERFORMANCE

Fig. 3.4: The X-ray diffraction patterns of SnO$_2$-RuO$_2$ composite films for samples, (a) S1 (3:2), (b) S2 (1:1), (c) S3 (3:1), and (d) S4 (2:3).

3.3.4 FT-IR studies

To characterize the SnO$_2$-RuO$_2$ composite material, we employed FT-IR spectroscopy, which is sensitive to short-range order in a compound. For the FT-IR study, SnO$_2$ and RuO$_2$ films were prepared by SILAR method. Fig. 3.6 shows the FT-IR spectra for SnO$_2$, RuO$_2$ and SnO$_2$-RuO$_2$ composite. Fig. 3.6 (a) shows the FT-IR spectrum of pure SnO$_2$ with peak at 643 cm$^{-1}$ which corresponds to the characteristic antisymmetric stretching vibrations for Sn-O-Sn [7]. In addition, broad bands observed at 3525 and 1085 cm$^{-1}$ are attributed to the O–H stretching vibrations [8]. The absorption peak observed at around 1650 cm$^{-1}$ may be due to the bending vibration of hydroxyl groups of molecular water [9]. The FT-IR
spectrum of RuO$_2$ is shown in Fig. 3.6 (b). For this, characteristic vibration peak for Ru-O-Ru is observed at 593 cm$^{-1}$ [10]. The peaks present at 3414, 1086 and 1624 cm$^{-1}$ corresponds to the O-H stretching vibrations and bending vibration of hydroxyl groups of molecular water. The less intense peak centered at 940 cm$^{-1}$ is assigned to characteristic stretching vibration of peroxo groups [11]. The FT-IR spectrum of SnO$_2$-RuO$_2$ composite (sample S3) is shown in Fig. 3.6 (c) from which it is observed that the characteristic vibration peak for SnO$_2$ is shifted to lower wavenumber compared with SnO$_2$ shown in Fig. 3.6 (a). This may be due to the presence of RuO$_2$ in SnO$_2$ matrix, Yuvuz and Gok was also observed the shifting of polyaniline peaks with the introduction of TiO$_2$ in the polyaniline-TiO$_2$ composite [12]. The O-H stretching vibrations (3416 and 1115 cm$^{-1}$), bending vibration of hydroxyl group of molecular water (1629 cm$^{-1}$) and peroxo groups (940 cm$^{-1}$) are also observed. Thus, the FT-IR studies ascertain the formation of SnO$_2$-RuO$_2$ composite.
Fig. 3.5: FT-IR spectra of (a) SnO$_2$, (b) RuO$_2$, and (c) SnO$_2$-RuO$_2$ composite (sample S3).

3.A.3.5 FT-Raman Studies

Raman scattering is a useful tool for the characterization of nanosized materials and a qualitative probe of the presence of lattice defects in solids [13]. At the same time, Raman spectroscopy is sensitive to crystal surface area. The typical Raman spectrum of SnO$_2$, RuO$_2$ and SnO$_2$-RuO$_2$ composite (sample S3) is shown in Fig. 3.6. The spectrum of SnO$_2$ (curve a) showed two peaks centered at 620 and 777 cm$^{-1}$ corresponding to the crystallites of SnO$_2$ with a tetragonal rutile structure (i.e. A$_{1g}$ and B$_{2g}$) [14]. The peak at 564 cm$^{-1}$ corresponds to amorphous SnO$_2$. The other peaks observed at 248 and 324 cm$^{-1}$ correspond to the N group vibration modes of SnO$_2$ nanocrystallites, which are referred to the large number of vacant lattice positions and local lattice disorders in the primary particulates [14]. On curve b in Fig. 3.6 two peaks observed at 526 and 640
cm\(^{-1}\) correspond to the \(E_g\) and \(A_{1g}\) vibration mode of RuO\(_2\) [15]. The peaks for SnO\(_2\)-RuO\(_2\) composite are shown in curve c in Fig. 3.6. In curve c, the peaks at 634 and 703 cm\(^{-1}\) correspond to crystalline RuO\(_2\) (i.e. \(A_{1g}\) and \(B_{2g}\)) in the rutile form, whereas as the peak at 558 cm\(^{-1}\) is due to the amorphous SnO\(_2\). In comparison with curve a and b in Fig. 3.6, the peak shifts in curve c for SnO\(_2\) and RuO\(_2\) are observed due to the quantum effects of decrease in particle size [16]. However, the certain new peaks observed in curve c, may be due to the SnO\(_2\)-RuO\(_2\) composite [17].

![FT-Raman spectra of (a) SnO\(_2\), (b) RuO\(_2\), and c) SnO\(_2\)-RuO\(_2\) composite (sample S3).](image)

**Fig. 3.6:** FT-Raman spectra of (a) SnO\(_2\), (b) RuO\(_2\), and c) SnO\(_2\)-RuO\(_2\) composite (sample S3).
3.3.6.3 Surface Morphological and Compositional Studies

The surface morphology of various composite films is studied using scanning electron microscopy (SEM). Fig. 3.7 (a) shows the surface morphology for pure SnO$_2$ and SnO$_2$-RuO$_2$ composite films. From the SEM image of SnO$_2$ for which irregular shaped agglomerates with porous morphology are observed. With the introduction of RuO$_2$ in the deposition, for sample S1 (Fig. 3.7 b) the morphology shows the large agglomerated crystallites. For sample S2, the surface is well covered with nanocrystallites and are arranged in such a way that, highly porous and fibrous structure is formed (Fig. 3.7 c). The SEM image of sample S3 (Fig. 3.7 d) showed the large agglomerates with comparatively smooth morphology. The SEM image for sample S4 is shown in Fig. 3.7 (e), from which the spherical nanograins covering entire substrate with less porous morphology are observed. The SEM study clearly denotes the porous and agglomerated morphology of pure SnO$_2$ is changed to less porous and granular morphology with the introduction of RuO$_2$ into SnO$_2$ matrix. The SEM images strongly confirmed the dependence of morphology of composite film on the SnO$_2$:RuO$_2$ cycle ratio. From the SEM studies It is seen that the composite film with higher RuO$_2$ content (sample S3) has smooth morphology with less porous structure, on the other hand, the composite with large SnO$_2$ content is highly porous (sample S1 and S2). It is observed that the addition of SnO$_2$ into RuO$_2$ increases the effective surface area of the net composite material. As confirmed from the structural studies, the samples S1 and S2 having crystallites in nanometer range resulted into high surface area by offering the porous morphology.
Fig. 3.7: The SEM image of (a) SnO$_2$ and SnO$_2$-RuO$_2$ composite films for (SnO$_2$:RuO$_2$) samples (b) S1 (3:2), (c) S2 (1:1), (d) S3 (1:3) and (e) S4 (2:3) at X10,000 magnification.
Fig. 3.8: The energy dispersive X-ray (EDAX) analyses of SnO$_2$-RuO$_2$ composite film (sample S3).

Fig. 3.8 shows typical EDAX pattern of the SnO$_2$-RuO$_2$ composite film (sample S3). The peaks for Sn, Ru and O are found in the spectrum. The formation of SnO$_2$-RuO$_2$ is confirmed from the EDAX spectrum. From the EDAX study it is observed that the composite film formed is in non-stoichiometric form. The Sn content in the sample is more compared with Ru, showing less Ru is involved in the composite formation. The observed atomic percentage for Sn, Ru and O is shown in Table 3.1.

Table 3.1: Elemental composition analyses of SnO$_2$-RuO$_2$ composite films

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<tr>
<th>Element</th>
<th>Atomic %</th>
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<td>O K</td>
<td>82.09</td>
</tr>
<tr>
<td>Ru L</td>
<td>1.58</td>
</tr>
<tr>
<td>Sn L</td>
<td>16.33</td>
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3.3.7 Surface Wettability Studies

The wetting behavior is characterized by the value of the contact angle, a microscopic parameter. If the wettability is high, contact angle ($\theta$),
will be small and the surface is hydrophilic. On the contrary, if the wettability is low, $\theta$ will be large and the surface is hydrophobic. Fig. 3.9 shows the water contact angle images of SnO$_2$–RuO$_2$ composite films for various cycle ratios. It is observed that for the composite sample S1 the water droplet flats on the surface, which means it is hydrophilic in nature with observed water contact angle of $\sim 13^0$. The hydrophilic nature of the surface may be due its nanocrystalline structure that supposed to possess high surface energy [18]. For the other samples from S2 to S4, a different wetting behavior is observed as compared to sample S1. The water contact angles observed for samples from S2 to S4 are greater than $90^0$ showing the hydrophobic behavior. From the SEM studies of these samples, it is observed that the morphology of sample S2 is fibrous and highly porous morphology. The air is trapped in such porous structure pushes the water drop upside, which is responsible for high water contact angle also the film composition may also responsible for its high water contact angle. The SEM images of sample S3 and S4 showed the porous but rough surface. Roughness is an important parameter in case of surface wettability as roughness increases, the surface with water contact angle $< 90^0$ becomes more hydrophilic and surface with water contact angle $>90^0$ becomes more hydrophobic [19]. From the study of water contact angle for sample S2, it is observed that the surface is becoming hydrophobic so increased roughness will surely increase the hydrophobicity which may be cause for getting higher contact angles for sample S3 and S4 [19].
Fig. 3.9: Contact angle images for SnO$_2$-RuO$_2$ composite films for (SnO$_2$:RuO$_2$) samples, (a) S1 (3:2), (b) S2 (1:1), (c) S3 (1:3) and (d) S4 (2:3).
SECTION B: SUPERCAPACITIVE PERFORMANCE OF TIN OXIDE RUTHENIUM OXIDE COMPOSITE THIN FILMS

3. B.1 Introduction

In the present work, SILAR deposited tin oxide ruthenium oxide (SnO$_2$-RuO$_2$) composite thin films have been used as supercapacitor electrodes. The supercapacitive performance of composite films with varying cycle ratio of SnO$_2$:RuO$_2$ have been studied by means of cyclic voltammetry and charge discharge cycling and optimized cycle ratio for SnO$_2$-RuO$_2$ deposition is found. Further, the effect of electrolyte concentration, deposited mass and scan rate on specific capacitance of optimized SnO$_2$-RuO$_2$ electrode have been investigated. In addition, stability performance and electrochemical impedance studies are carried out.

3. B.2. Experimental Details to find Supercapacitive Properties

3. B.2.1 Cyclic Voltammetry

Cyclic voltammetry provides a measure of a supercapacitor's charge-response with regard to a changing voltage, and is therefore a means of evaluating capacitance. To perform cyclic voltammetry tests a series of changing voltages at a constant sweep rate (dV/dt) is applied and the response current is recorded. The cyclic voltammetry (CV) experiments were performed using 263-A EG & G, Applied Research Potentiostat to determine the specific capacitance of the SnO$_2$-RuO$_2$ composite electrodes in H$_2$SO$_4$ electrolyte. The capacitance ‘C’ of film was calculated from the relation,

$$C = \frac{\int I}{(dV/dt)}$$  \hspace{1cm} (3.6)

Where, ‘$\int I$’ is the average current in amperes measured by integrating the current under the CV curve and (dV/dt) is the scan rate in
mV.s\(^{-1}\). Similarly, the interfacial capacitance \(C_i\) is obtained by dividing the capacitance by respective electrode area in the electrolyte.

\[
C_i = \frac{C}{A}
\]  

(3.7)

Where ‘A’ is, the area (1 cm\(^2\) in this study) of electrode dipped in the electrolyte. The specific capacitance \(C_s\) of the electrode is obtained by dividing the capacitance by the weight of SnO\(_2\)-RuO\(_2\) composite electrode dipped in the electrolyte.

\[
C_s = \frac{C}{W}
\]  

(3.8)

Where, ‘W’ is the weight of the SnO\(_2\)-RuO\(_2\) composite electrode dipped in the electrolyte.

3.B.2.2 Charge-discharge Study

A method of evaluating a supercapacitor’s energy and power densities is to perform constant current charging. Charging or discharging the cell at constant current results in a voltage response from which different parameters such as average capacitance, coulomb efficiency, specific energy density and power density of the electrode can be calculated. The charge-discharge analysis was performed by WonATech Automatic Battery Cycler WBCS system, interfaced to a computer.

The average capacitance of the electrode was calculated according to the following equation [20],

\[
C = I \times \left(\frac{\Delta t}{\Delta V}\right)
\]  

(3.9)

Where, ‘I’ (A) is the constant current, ‘\(\Delta t\)’ is the time duration (second) of the discharge process and ‘\(\Delta V\)’ (V) is the voltage range.

The specific energy density and power density are calculated from the following equations, [21].

Specific energy (SE) = \(Q \times \left(\frac{\Delta V}{W}\right) = \frac{I \times t \times \Delta V}{W}\)  

(3.10)
Specific power \((SP)\) = \(\frac{SE}{t} = \frac{I \times \Delta V}{W}\) \[ (3.11) \]

Where, \(W\) is the mass \((\text{Kg})\) of electrode material.

**3.B.2.3 Electrochemical Impedance Spectroscopy**

Impedance spectroscopy is a powerful method of evaluating a component's performance in the frequency domain. Special equipment is required to apply a small AC voltage and measure the changes in magnitude and phase over a range of frequencies. The frequency range used was from \(10^{-2}\) to \(10^5\) Hz at open circuit voltage. The electrochemical impedance measurements were conducted with a versastat 3G frequency response analyzer (FRA) under Zplot program (Scribner Associates Inc.).

**3.B.2.4 Experimental Setup for Supercapacitor Study**

Fig. 3.10 (a) shows the schematic of experimental set up and (b) shows the actual experimental set up for the supercapacitor study. The electrochemical measurements for supercapacitor were carried out in a three electrode electrochemical cell, in which the \(\text{SnO}_2\)-\(\text{RuO}_2\) composite electrode was used as the working electrode, platinum as the counter, and saturated calomel electrode (SCE) as the reference electrode.
Fig. 3.10 (a) Schematic and (b) actual experimental set up for the supercapacitor study.
3.B.3 Results and Discussion

3.B.3.1 Effect of Variation of Cycle Ratio of SnO$_2$:RuO$_2$ Deposition

Typical cyclic voltammetric behavior of pure SnO$_2$ and SnO$_2$-RuO$_2$ composite films measured in 0.5 M H$_2$SO$_4$ electrolyte in the potential range of -0.2 to +0.6 V vs. SCE at 5 mV.s$^{-1}$ scan rate is shown in Fig. 3.11. The CV curve for pure SnO$_2$ shows a negligible current response in microamperes. The CV curve for SnO$_2$ purely shows double layer capacitance due to the absence of redox transitions in the given potential region. The observed double layer capacitance for SnO$_2$ is about ~4 F.g$^{-1}$ that is very small and can be neglected. Therefore, the pseudocapacitance coming from SnO$_2$-RuO$_2$ composite thin film is mainly attributed to the RuO$_2$. The increase in the current response is observed only after the introduction of RuO$_2$ into SnO$_2$. The CV curves for the composites shows that the characteristic of the capacitance is different from that of the electric double-layer capacitance, in which the CV curve is close to the ideal rectangular shape. The present results imply that the measured capacitance of composite is mainly associated with the redox mechanism. From a comparison of curves (b) to (e) in Fig. 3.11, an obvious decrease in the voltammetric current and less symmetric I-V curves are found when the SnO$_2$ content is increased. The small capacitive current measured for potentials below +0.4 V vs. SCE is commonly attributed to the high density of bound water and OH$^-$ formed on the surface of RuO$_2$ particles [22]. This water plays the role of a potential barrier for the electrons hindering the electron hopping process between the particles of the material.

A low specific capacitance of 9 F.g$^{-1}$ is observed for the sample S1 (2:3). The specific capacitance is increased to 24 F.g$^{-1}$ for the sample S2. The highest specific capacitance of 185 F.g$^{-1}$ is observed for sample S3 (1:3). From the electrochemical studies, it is observed that the specific capacitance of the composite electrode is highly dependent on the
presence active material in the sample. As SnO₂ is inactive in the given potential range (-0.2 to +0.6 V vs. SCE), only active material is RuO₂, the sufficient presence of active material enhances the specific capacitance value. For sample S1, the low specific capacitance value is due to the probability of deficiency of active material i.e. RuO₂. The large specific capacitance value of 185 F.g⁻¹ is observed for the sample S3 as the presence of RuO₂ in the sample S3 is large.

![Diagram](image)

**Fig. 3.11:** The CV curves of (a) SnO₂ and SnO₂-RuO₂ composite electrodes for (SnO₂:RuO₂) samples (b) S1, (c) S2, (d) S3 and (S4) in the potential range of -0.2 to +0.6 V vs.SCE at 5 mV.s⁻¹ scan rate.

### 3.B.3.2 Charge-discharge Studies

The charge–discharge behavior of the samples (S1, S2, S3 and S4) is examined by chronopotentiometry from -0.2 to +0.6 V vs. SCE at the current density of 1 mA.cm⁻² in 0.5 M H₂SO₄ electrolyte as shown in Fig. 3.12. The discharge profile usually contains two parts, first a resistive
component arising from the sudden voltage drop representing the voltage change due to the internal resistance and a capacitive component related to the voltage change related to change in energy within the capacitor. An IR drop is observed in each sample, which is attributed to the internal resistance of the electrode material. It is observed that the IR drop is more for samples S1 and S2 and is decreased for samples S3 and S4. As it is well known that, the SnO$_2$ is highly resistive and RuO$_2$ has metallic conductivity, the large IR drop (421 mV) observed for sample S1 (3:2) (Fig. 3.12 a), may be due to the large SnO$_2$ content. Comparatively less IR drop (91 mV) is observed for sample S3 (1:3) (Fig. 3.12 c) which may be due to the large RuO$_2$ content in the sample. The Ragone plot for composite samples is shown in Fig. 3.13. The values of specific power (SP) and specific energy (SE) is calculated for all samples lie in the Ragone plot typically calculated for supercapacitors[23]. The sample S3 showed good discharging behavior with large discharge time compared with other samples, which is responsible for its high specific energy. The sample S3 (1:3) exhibit the high SP of 0.839 kW.Kg$^{-1}$ and high SE of 11.18 Wh.Kg$^{-1}$, making it promising electrode material in supercapacitor application.
Fig. 3.12: The charge-discharge curves of SnO$_2$-RuO$_2$ composite electrodes for (SnO$_2$:RuO$_2$) samples, a) S1 (3:2), b) S2 (1:1), c) S3 (1:3) and d) S4 (2:3) in the potential range of -0.2 to 0.6 V vs. SCE at the current density of 1 mA.cm$^{-2}$. 

**CHAPTER- III: SYNTHESIS AND CHARACTERIZATION OF TIN OXIDE RUTHENIUM OXIDE COMPOSITE THIN FILMS BY SUCCESSIVE IONIC LAYER ADSORPTION AND REACTION (SILAR) METHOD AND THEIR SUPERCAPACITIVE PERFORMANCE**
CHAPTER III: SYNTHESIS AND CHARACTERIZATION OF TIN OXIDE RUTHENIUM OXIDE COMPOSITE THIN FILMS BY SUCCESSIVE IONIC LAYER ADSORPTION AND REACTION (SILAR) METHOD AND THEIR SUPERCAPACITIVE PERFORMANCE

**Fig. 3.13:** The Ragone plot for SnO$_2$-RuO$_2$ composite electrodes for (SnO$_2$:RuO$_2$) samples, S1 (3:2), b) S2 (1:1), c) S3 (1:3) and d) S4 (2:3).

3.B.3.3 Effect of Electrolyte Concentration

The capacitance origin in an electrode can be evaluated by studying its CV performance using different concentration of electrolyte. If the capacitance originated is purely due to pseudocapacitance then there is no any change in value of capacitance with the electrolyte concentration. However, if the capacitance originated is from double layer mechanism the change in the electrolyte concentration will have a direct effect on the capacitance value [24]. The effect of electrolyte concentration on the supercapacitive performance of SnO$_2$-RuO$_2$ composite (sample S3) was studied at a scan of 20 mV.s$^{-1}$ within the potential range of -0.2 to +0.6 V vs. SCE. Fig. 3.14 (a) shows the CV curves of composite electrode in different concentrations of H$_2$SO$_4$ electrolyte (i.e. from 0.1 to 1 M). The current under the CV curve increases as the H$_2$SO$_4$ concentration is increased from
0.1 to 0.5 M. This indicates the specific capacitance arises in the present study is the contribution of both double layer and pseudocapacitance [24]. Fig. 3.14 (b) shows the variation of specific capacitance with concentration of H₂SO₄ electrolyte. The specific capacitance increased from 53 to 66 F.g⁻¹ as concentration of electrolyte is varied from 0.1 to 0.5 M. Above this concentration, decrease in specific capacitance is observed. Due to the increase in electrolyte concentration, conductivity of ions decreased which causes increase in electrochemical resistance near the surface of electrode resulting in less current response [25].

**Fig. 3.14 (a):** CV curves of SnO₂-RuO₂ composite electrode (sample S3) in different H₂SO₄ concentrations at 20 mV.s⁻¹ scan rate.
Fig. 3.14 (b): The variation of specific capacitance of SnO$_2$-RuO$_2$ composite electrode (sample S3) with concentration of H$_2$SO$_4$ electrolyte.

3.B.3.4 Effect of Film Thickness

The coverage or thin film thickness plays an important role in the supercapacitor study. The thickness of SnO$_2$-RuO$_2$ composite (sample S3) was varied by varying the total deposition cycles. The thickness of SnO$_2$-RuO$_2$ composite film was measured by gravimetric weight difference method in terms of weight of SnO$_2$-RuO$_2$ deposited on the stainless steel substrate per unit area (mg.cm$^{-2}$). Effect of deposited weight of SnO$_2$-RuO$_2$ composite film (sample S3) on specific and interfacial capacitances was studied in 0.5 M H$_2$SO$_4$ electrolyte at 5 mV.s$^{-1}$ scan rate. Fig. 3.15 (a) shows the variation of cyclic voltammogram as a function of weight of deposited material in 0.5 M H$_2$SO$_4$ electrolyte. Fig. 3.15 (b) shows the variation of specific and interfacial capacitances with deposited weight of SnO$_2$-RuO$_2$.
(sample S3) composite film. The increased current response with increase in deposited weight shows that the voltammetric charge of the SnO$_2$-RuO$_2$ films also increases with film thickness. The interfacial capacitance increased from 0.0314 to 0.18 F.cm$^{-2}$ and specific capacitance increased from 90 to 184 F.g$^{-1}$ with increase in deposited weight up to its critical value, above which there is decrease in the values of both. Patil $et$ $al.$ reported similar type of increasing trend for interfacial and specific capacitances with deposited weight [26]. Park $et$ $al.$ [5] however, observed a decreasing trend of capacitance with loaded weight of RuO$_2$ material. The increasing trend observed in the present case may be due to the less value of critical deposited weight. Above the critical value of deposited weight, the decrease in the interfacial capacitance and specific capacitance values are observed which may be due to the less porous morphology and resistance offered by SnO$_2$ particles. At lower value of film thickness, there are small number of active sites present for the protonation (i.e. adsorption and de-adsorption of protons) process which results into low specific capacitance value. When the weight of the electrode increased more than the critical weight (0.953 mg.cm$^2$ here), the inner layers became inactive and remained as the dead volume [27].
**Fig. 3.15 (a):** The variation of CV curves with weight of deposited material of SnO$_2$-RuO$_2$ composite (sample S3), in 0.5 M H$_2$SO$_4$ electrolyte at 5 mV.s$^{-1}$ scan rate.
Fig. 3.15 (b): The variation of interfacial and specific capacitance of SnO$_2$-RuO$_2$ composite electrode (sample S3) with weight of deposited material.

3.B.3.5 Effect of Scan Rate

Fig. 3.16 (a) shows the effect of scan rate on SnO$_2$-RuO$_2$ composite electrode (sample S3) with 0.953 mg.cm$^{-2}$ film thickness. The shape of the CV curve at higher scan rate is different from that at lower scan rate. For SnO$_2$-RuO$_2$, composite electrode, symmetrical CV curves are obtained at low scan rate because the oxidation and reduction currents are of the same magnitude. Zheng observed the similar behavior of change in CV shape at lower and higher scan rates [28]. Fig. 3.16 (b) shows the variation of specific and interfacial capacitances, with the scan rate. From the graph, it is seen that the specific and interfacial capacitances are decreased from 183 F.g$^{-1}$ and 0.18 F.cm$^{-2}$ to 43 F.g$^{-1}$ and 0.04 F.cm$^{-2}$, respectively, as the scan rate is increased from 5 to 150 mVs$^{-1}$. 
The decrease in capacitance at higher scan rate is attributed to the inactive inner active sites involved in the redox transitions, probably due to the diffusion effect of proton within the electrode [23]. The decreasing trend of the capacitance suggests that the parts of the surface of electrode are inaccessible at high charging–discharging rate. Hence, the specific capacitance obtained at the slowest scan rate is believed to be close to that of full utilization of the electrode material. The lower scan rate allows more time for the proton to access the bulk of the oxide.

Fig. 3.16 (a): The CV curves of SnO$_2$-RuO$_2$ composite electrode (sample S3) at different scan rates in 0.5 M H$_2$SO$_4$ electrolyte.
3.3.6 Stability Studies

Cycle life (stability) of SnO$_2$-RuO$_2$ composite electrode in 0.5 M H$_2$SO$_4$ electrolyte was tested by CV. Fig. 3.17 (a) shows the CV curves of SnO$_2$-RuO$_2$ composite electrode at the scan rate of 100 mV.s$^{-1}$ within the voltage range -0.2 to +0.6 V vs. SCE, after different number of cycles. It was found that current under the curve decreased after 500 cycles above which the decreasing trend of current is observed uptil 2000 cycles and above which there was a negligible loss in the current (not shown). The decrease in specific capacitance with different cycle numbers is shown in Fig. 3.17 (b). As revealed from the Fig. 3.17 (b), the specific capacitance decreased from 45 to 39 F.g$^{-1}$ with increasing in cycle numbers to 2000 cycles demonstrating 85% capacitance retained ratio. This behavior is because; the active material may be lost, due to the dissolution and/or detachment, during the early charging/discharging cycles in the electrolyte. It would
consequently render the specific capacitance decay of the electrode [29]. From the stability study, stable nature of SnO$_2$-RuO$_2$ electrode is observed which would be useful in energy storage applications.

Fig. 3.17 (a): CV curves for SnO$_2$-RuO$_2$ composite electrode (sample S3) at various cycle numbers in 0.5 M H$_2$SO$_4$ electrolyte at 100 mV.s$^{-1}$ scan rate.
3.B.3.7 Electrochemical Impedance Analysis

In order to investigate the electrochemical characteristics of the electrode and electrolyte in quantitative manner impedance measurement was performed. The electrochemical impedance measurement (at open circuit voltage, in the frequency range $10^5$ to $10^{-2}$ Hz) of SnO$_2$-RuO$_2$ composite (sample S3) was carried out in 0.5 M H$_2$SO$_4$. The Nyquist depictions ($Z'$ vs. $Z''$) of the raw impedance data for the is shown in Fig. 3.18. For the convenience of the interpretation, this plot can be divided into high and low frequency regions. The frequency at which there is deviation from the semicircle is known as ‘knee’ frequency, which reflects the maximum frequency at which capacitive behavior is dominant. The presence of semicircle in the high frequency region suggests that there is a charge transfer resistance, while the straight line in the low frequency
region angled of the ~ 45° to the real axis is attributed to the capacitive behavior. Inset (Fig. 3.18) shows the expanded high frequency region of the same plot. This implies that the supercapacitor shows a blocking behavior at high frequencies and capacitive behavior at low frequencies [30-32]. The 24 Ω, high frequency impedance intercept reflects the equivalent series resistance (ESR) of the electrolyte.

Bode representation of this data is shown in the Fig. 3.19. The Bode plot at a phase angles of 34 and 82° gives about 82% and 23% of the power correspond to the heat production at the internal resistance. The loss factors of electrode 0.23 and 1.48 are calculated in the lower and higher frequency region respectively. The relaxation time constant ($\tau_0$), calculated (plots of $C''(\omega)$ vs. frequency) is shown in Fig. 3.20. Relaxation time ($\tau_0$) for the sample S3 is found to be 0.86 s. The $\tau_0$ is a very important factor, which decides applicability of electrode material according to energy demand. Small relaxation time constant value exhibits a fast energy release capability of the electrode, to provide higher power density [33].
Fig. 3.18: Nyquist plot of SnO$_2$-RuO$_2$ composite (sample S3) in 0.5 M H$_2$SO$_4$. 
Fig. 3.19: Bode plot of SnO$_2$-RuO$_2$ composite (sample S3) in 0.5 M H$_2$SO$_4$. 
Fig. 3.20: Plot of real capacitance \( (C') \) vs. frequency for SnO\(_2\)-RuO\(_2\) composite (sample S3).

Conclusions

In conclusion, SnO\(_2\)-RuO\(_2\) composite films have been successfully synthesized by SILAR method. The nanocrystalline nature of the composite film for SnO\(_2\) enriched sample changed to amorphous for RuO\(_2\) enriched sample. The highly porous structure observed for samples with large SnO\(_2\) content, becomes less porous for samples with large RuO\(_2\) content. The ESR power corresponds to heat production due to internal resistance of SnO\(_2\)-RuO\(_2\) composite restricts maximum capacitance to 183 F.g\(^{-1}\). The maximum specific power of 0.839 kW.Kg\(^{-1}\) and specific energy of 11.18 Wh.Kg\(^{-1}\) is observed for SnO\(_2\)-RuO\(_2\) composite with good cycle life. Thus, SILAR method is proved as reliable method for deposition of SnO\(_2\)-RuO\(_2\) composite films with promising supercapacitive properties.
References

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