## CHAPTER-IV

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Title</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>SECTION A</strong> SYNTHESIS AND CHARACTERIZATION OF TIN OXIDE RUTHENIUM OXIDE COMPOSITE FILMS BY CHEMICAL BATH DEPOSITION (CBD) METHOD</td>
<td></td>
</tr>
<tr>
<td>4.A.1</td>
<td>Introduction</td>
<td>117</td>
</tr>
<tr>
<td>4.A.2</td>
<td>Experimental Details</td>
<td>118</td>
</tr>
<tr>
<td>4.A.2.1</td>
<td>Substrate Cleaning</td>
<td>118</td>
</tr>
<tr>
<td>4.A.2.2</td>
<td>Solution Preparation</td>
<td>118</td>
</tr>
<tr>
<td>4.A.2.3</td>
<td>Experimental Setup for the Deposition of Tin Oxide-Ruthenium Oxide (SnO$_2$-RuO$_2$) Composite Thin Films by CBD Method</td>
<td>118</td>
</tr>
<tr>
<td>4.A.2.4</td>
<td>Characterization Techniques</td>
<td>120</td>
</tr>
<tr>
<td>4.A.3</td>
<td>Results and Discussion</td>
<td>120</td>
</tr>
<tr>
<td>4.A.3.1</td>
<td>Reaction Mechanism of SnO$_2$-RuO$_2$ Composite Film Formation</td>
<td>120</td>
</tr>
<tr>
<td>4.A.3.2</td>
<td>Thickness Measurement</td>
<td>121</td>
</tr>
<tr>
<td>4.A.3.3</td>
<td>Structural Studies</td>
<td>122</td>
</tr>
<tr>
<td>4.A.3.4</td>
<td>FT-IR Studies</td>
<td>123</td>
</tr>
<tr>
<td>4.A.3.5</td>
<td>FT-Raman Studies</td>
<td>124</td>
</tr>
<tr>
<td>4.A.3.6</td>
<td>Surface Morphological and Compositional Studies</td>
<td>128</td>
</tr>
<tr>
<td>4.A.3.7</td>
<td>Surface Wettability Studies</td>
<td>129</td>
</tr>
</tbody>
</table>
## SECTION B
### SUPERCAPACITIVE PERFORMANCE OF TIN OXIDE RUTHENIUM OXIDE COMPOSITE THIN FILMS

<table>
<thead>
<tr>
<th>4.B.1</th>
<th>Introduction</th>
<th>130</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.B.2.</td>
<td>Experimental Details to find Supercapacitive Properties</td>
<td></td>
</tr>
<tr>
<td>4.B.3</td>
<td>Results and Discussion</td>
<td></td>
</tr>
<tr>
<td>4.B.3.1</td>
<td>Effect of Variation of Vol.% of RuCl₃ in Deposition</td>
<td>130</td>
</tr>
<tr>
<td>4.B.3.2</td>
<td>Charge-discharge studies</td>
<td>132</td>
</tr>
<tr>
<td>4.B.3.3</td>
<td>Effect of Electrolyte Concentration</td>
<td>134</td>
</tr>
<tr>
<td>4.B.3.4</td>
<td>Effect of Film Thickness</td>
<td>136</td>
</tr>
<tr>
<td>4.B.3.5</td>
<td>Effect of Scan Rate</td>
<td>138</td>
</tr>
<tr>
<td>4.B.3.6</td>
<td>Stability Studies</td>
<td>140</td>
</tr>
<tr>
<td>4.B.3.7</td>
<td>Electrochemical Impedance Analysis</td>
<td>142</td>
</tr>
<tr>
<td></td>
<td>Conclusions</td>
<td>146</td>
</tr>
<tr>
<td></td>
<td>References</td>
<td>147</td>
</tr>
</tbody>
</table>
SECTION A: SYNTHESIS AND CHARACTERIZATION OF TIN OXIDE RUTHENIUM OXIDE COMPOSITE THIN FILMS BY CHEMICAL BATH DEPOSITION (CBD) METHOD

4.A.1 Introduction

The methods used for deposition of SnO$_2$-RuO$_2$ composite electrodes are sol-gel, hydrothermal and sputtering [1-3]. It is well known that the supercapacitive performance of electrode could be improved by changing its morphology, on this basis new methods for preparation of SnO$_2$-RuO$_2$ composite electrodes are desirable. The use of low temperature solution based methods will be promising as these methods are cheap and simple. Among the various low temperature solution based methods chemical bath deposition (CBD) is the most attracting method.

The CBD method has been used to deposit films of metal sulfides, selenides and oxides, together with some miscellaneous compounds. CBD is an excellent method to deposit nanocrystalline thin films [4]. CBD refers deposition from solution, (generally aqueous) where the required deposit is both, chemically generated and deposited in the same bath. The CBD method is based on the slow controlled precipitation of the desired compound from its ions from reaction bath solution on the substrate surface. In CBD, substrate can be coated with desired material directly, which is an advantage over the methods in which final product is in powder form. The method is also useful for large area deposition. More study on metal oxide films deposited by CBD is explored by Pawar et. al.[5]. However, little work is done on deposition of composite films by CBD [6].

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

4.A.2 Experimental Details

4.A.2.1 Substrate Cleaning

The stainless steel substrates were used for deposition of SnO$_2$-RuO$_2$ composite thin films. The substrates were cleaned according to the procedure described in section 3.A.2.1.

4.A.2.2 Solution Preparation

In the present work, stannic chloride (Sn(IV)Cl$_4$), ruthenium chloride (Ru(III)Cl$_3$) and urea (NH$_2$CONH$_2$) solutions have been prepared in double distilled water as sources of Sn$^{4+}$, Ru$^{3+}$ and OH$^-$ ions, respectively, for the deposition of SnO$_2$-RuO$_2$ composite films.

4.A.2.3 Experimental Setup for the Deposition of SnO$_2$-RuO$_2$ Composite Thin Films by CBD Method

Fig. 4.1 (a, b) shows the schematic and actual experimental setup for deposition of SnO$_2$-RuO$_2$ composite films.
Chapter IV: Synthesis and Characterization of Tin Oxide Ruthenium Oxide Composite Thin Films by Chemical Bath Deposition (CBD) Method and Their Supercapacitive Performance

Fig. 4.1 (a): Schematic and (b) actual experimental setup for chemical bath deposition (CBD) of SnO$_2$-RuO$_2$ composite thin films

In typical synthesis, the mixed solution of 0.05 M stannic (Sn$^{4+}$) chloride and 0.01 M ruthenium (Ru$^{3+}$) chloride solution was taken and pH of the solution adjusted in the range of 1–2 using urea (NH$_2$CONH$_2$) solution with a constant stirring. The stainless steel substrates were immersed vertically in the above bath and the bath was heated at 353 K. After 10 min, the precipitation was started in the bath and during the precipitation, heterogeneous reaction occurred and deposition of SnO$_2$-RuO$_2$ film took place on the substrates. The substrates coated with SnO$_2$-RuO$_2$ thin film were removed after 2 h, washed with double distilled water and air dried. In order to vary the amount of RuO$_2$ in the deposition bath, the volume percentage of RuCl$_3$ in the deposition bath is varied as 5, 10, 15 and 20% the corresponding composite films are named as C1, C2, C3 and C4, respectively and used in further studies. Fig. 4.2 shows the photograph of SnO$_2$-RuO$_2$ composite films for various vol.% of RuCl$_3$ in the deposition
bath on the stainless steel substrates (> 8 cm²) proving the usefulness of CBD method for large area deposition. The films prepared were uniform, blackish in color and well adherent to the substrate.

![Fig. 4.2: Photograph of SnO₂-RuO₂ composite thin films deposited by CBD by varying volume of RuCl₃ (5, 10, 15 and 20%) in deposition on stainless steel substrates (>8 cm² area).](image)

**4.A.2.4 Characterization Techniques**

The different characterization techniques used to characterize structural, morphological, compositional and wettability properties are described in section 3.A.2.5.

**4.A.3 Results and Discussion**

**4.A.3.1 Reaction Mechanism of SnO₂-RuO₂ Composite Film Formation**

The chemical reaction of SnO₂-RuO₂ composite film formation can be enlightened as follows. The primary role of urea is to provide a slow controlled supply of OH⁻ ions through slow thermal decomposition [17].

\[
\text{CO(NH}_2\text{)}_2 + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{NH}_3
\]  

(4.1)

In aqueous solution, ammonia slowly releases the OH⁻ ions as,
\[ \text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^- \] (4.2)

The Sn$^{4+}$ ions in the solution reacts with OH$^-$ ions to form stannic hydroxide (Sn(OH)$_4$) which then hydrolyzed to give SnO$_2$ through the reaction,

\[ \text{Sn}^{4+} + 4\text{OH}^- \rightarrow \text{Sn(OH)}_4 \rightarrow \text{SnO}_2 + \text{H}_2\text{O} \] (4.3)

Similarly, the Ru$^{3+}$ ions reacts with OH$^-$ ions in the solution to form ruthenium hydroxide (Ru(OH)$_3$) which then react with excess OH$^-$ ions to form RuO$_2$ as,

\[ \text{Ru}^{3+} + 3\text{OH}^- \rightarrow \text{Ru(OH)}_3 \] (4.4)

\[ \text{Ru(OH)}_3 + \text{OH}^- \rightarrow \text{RuO}_2 + 2\text{H}_2\text{O} \] (4.5)

This describes the SnO$_2$-RuO$_2$ film formation mechanism by CBD. To prepare SnO$_2$-RuO$_2$ composite thin films with varying composition of RuO$_2$, the vol.% of RuCl$_3$ in the deposition is varied from 5 to 20%.

4.A.3.2 Thickness Measurement

The film thickness was determined gravimetrically in terms of weight of the deposited material per unit area. Fig. 4.3 shows the variation of thickness (mg.cm$^{-2}$) of SnO$_2$-RuO$_2$ composite films (samples C1 to C4). From the graph, it is observed that the thickness increases with increase in the volume of RuCl$_3$ in the bath. The maximum thickness (mg.cm$^{-2}$) of 0.52 mg. cm$^{-2}$ is observed for sample C4 (20 vol.% of RuCl$_3$). Such behavior can be understood by film formation and continuous precipitation in the bulk of solution [8].
Fig. 4.3: Variation of film thickness of SnO$_2$-RuO$_2$ composite film with variation of volume (5, 10, 15 and 20 vol.%) of RuCl$_3$ solution.

4.3.3 Structural Studies

The X-ray diffraction (XRD) patterns of SnO$_2$-RuO$_2$ composite films are presented in Fig. 4.4. The XRD patterns contain no diffraction peaks other than corresponding to the stainless substrate. The less intensity of stainless steel peaks observed for sample C4 (Fig. 4.4 d) is may be due to its high thickness compared with other samples. Thus, the XRD studies confirmed the formation of amorphous nature of SnO$_2$-RuO$_2$ composite film. The amorphous phase for SnO$_2$-RuO$_2$ composite was also observed by Yanqun and Dian [9] and Hu et. al. using sol-gel method [1]. The amorphous phase is suitable for electrochemical applications, since the protons can easily permeate through the bulk of the amorphous electrode and whole amount of electrode is utilized [10].
4.A.3.4 FT-IR Studies

The FT-IR absorption spectra of SnO$_2$, RuO$_2$ and SnO$_2$-RuO$_2$ composite (sample C3) deposited by CBD are shown in Fig.4.5. The FT-IR spectrum of SnO$_2$ showed strong band at 674 cm$^{-1}$ corresponding to the characteristic antisymmetric stretching vibrations for Sn-O-Sn [11]. The shoulder of this band at 610 cm$^{-1}$ corresponds to the characteristic stretching vibrations of Sn-O [12]. In addition, the broad bands at 3400 and 1020 cm$^{-1}$ observed which are attributed to the O–H stretching vibrations [13]. The absorption peak at around 1633 cm$^{-1}$ is due to the bending vibration of hydroxyl groups of molecular water [14]. The FT-IR spectrum of pure RuO$_2$ is shown in Fig. 4.5 (b). The characteristic vibration peak for Ru-O is observed at 612 cm$^{-1}$ [15]. The peaks present at 3410,
1015 and 1627 cm\(^{-1}\) correspond to the O-H stretching vibrations and bending vibration of hydroxyl groups of molecular water, respectively. The FT-IR spectrum of SnO\(_2\)-RuO\(_2\) composite (sample C3) is shown in Fig. 4.5 (c). It is observed that the sharp peak for antisymmetric stretching of Sn-O-Sn is weakened in SnO\(_2\)-RuO\(_2\) composite. In addition, the characteristic vibration band of Sn-O is shifted to lower wavenumber (580 cm\(^{-1}\)) compared to the pure SnO\(_2\) (610 cm\(^{-1}\)). This indicates the RuO\(_2\) is incorporated with SnO\(_2\) successfully [16].

![FT-IR spectra of SnO\(_2\), RuO\(_2\) and SnO\(_2\)-RuO\(_2\) composite](image)

**Fig. 4.5:** FT-IR spectra of (a) SnO\(_2\), (b) RuO\(_2\) and (c) SnO\(_2\)-RuO\(_2\) composite (sample C3).

### 4.A.3.5 FT-Raman Studies

The typical Raman spectra of CBD deposited SnO\(_2\), RuO\(_2\) and SnO\(_2\)-RuO\(_2\) composite (sample C3) are shown in Fig. 4.6. The Raman spectrum of SnO\(_2\) (Fig. 4.6 a) showed peak centered at 763 cm\(^{-1}\) corresponding to the crystallites of SnO\(_2\) with a tetragonal rutile structure for B\(_{2g}\) vibration [17].
The Raman peak at 589 cm\(^{-1}\) corresponds to amorphous SnO\(_2\). The other Raman peaks observed at 320 and 436 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 [17]. The Raman spectrum of RuO\(_2\) (Fig. 4.6 b) showed two Raman peaks at 622 and 685 cm\(^{-1}\) correspond to the A\(_{1g}\) and B\(_{2g}\) vibration modes of RuO\(_2\) [18]. Fig. 4.6 (c) shows the Raman spectrum for SnO\(_2\)-RuO\(_2\) composite. The peak at 668 cm\(^{-1}\) corresponds to crystalline RuO\(_2\) (i.e. B\(_{2g}\)) in the rutile form, whereas as the Raman peak at 564 cm\(^{-1}\) is due to the amorphous SnO\(_2\). In comparison with curves (a) and (b) in Fig. 4.6, the shift in peak positions in curve c for SnO\(_2\) and RuO\(_2\) are observed due to the quantum effects of decrease in particle size [19]. The certain new peaks observed in Fig. 4.6 (c) for composite may be due to SnO\(_2\)-RuO\(_2\) composite [2].
Fig. 4.6: FT-Raman spectra of (a) SnO$_2$, (b) RuO$_2$ and (c) SnO$_2$-RuO$_2$ composite (sample C3).

4.A.3.6 Surface Morphological and Compositional Studies

The SEM images of pure SnO$_2$ and SnO$_2$–RuO$_2$ composite samples are shown in Fig. 4.7. The SEM image for SnO$_2$ is shown in Fig. 4.7 (a), which revealed the smooth and compact morphology. It is observed the smooth and compact morphology of pure SnO$_2$ changed to rough and interconnected network like with overgrowth structure for sample C1 (Fig. 4.7 b). With further increment of RuCl$_3$ in the deposition, the network structure becomes relatively compact with small pits and cracks on the surface for sample C2 (Fig. 4.7 c). The small pits observed becomes larger and irregularly shaped with further addition of RuCl$_3$ for sample C3 (Fig. 4.7 d), the size of the pits however decreased with more RuCl$_3$ in the
deposition and surface becomes rough and elongated structure like for sample C4 (Fig. 4.7 e). The SEM studies clearly shows the transition of smooth and compact morphology of pure SnO$_2$ to the rough surface with irregular pits and elongated structure with addition of RuCl$_3$ in the deposition. This may be due to different growth kinetics associated with the variation in the composition of bath for deposition.

Fig. 4.7: The SEM images of (a) SnO$_2$ and SnO$_2$-RuO$_2$ composite films for samples, (b) C1 (5%), (c) C2 (10%), (d) C3 (15%) and (e) S4 (20%) at X3,000 magnification.
Fig. 4.8: The energy dispersive X-ray (EDAX) analysis of SnO$_2$-RuO$_2$ composite film (sample C3).

Fig. 4.8 shows typical EDAX pattern of the SnO$_2$-RuO$_2$ composite film (sample C3). The peaks for Sn, Ru and O were present in the spectrum confirming the formation of SnO$_2$-RuO$_2$ composite. The observed atomic percentages for Sn, Ru and O are shown in Table 4.1, which showed the SnO$_2$-RuO$_2$ composite film is in non-stoichiometric form.

**Table 4.1:** Elemental composition analyses of SnO$_2$-RuO$_2$ composite (sample C3) film

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<thead>
<tr>
<th>Element</th>
<th>Atomic %</th>
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</thead>
<tbody>
<tr>
<td>O K</td>
<td>67.01</td>
</tr>
<tr>
<td>Ru L</td>
<td>20.67</td>
</tr>
<tr>
<td>Sn L</td>
<td>12.32</td>
</tr>
</tbody>
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4.A.3.7 Surface Wettability Studies

Wettability involves the interaction between solid, liquid and vapor interface. Both highly hydrophilic and hydrophobic surfaces are important for practical application [20]. Fig. 4.9 (a) to (d) shows the water contact angle images for SnO$_2$-RuO$_2$ composite films for samples C1 to C4, respectively. From the images, it was observed that the water drop lies flat
on the surface instead of forming a water droplet, which proves the hydrophilic nature of composite films. For all samples (C1 to C4), there is no appreciable change in shape of water drop and the water contact angles lies in between 12 to 16°. Generally, the surface with high specific energy has lower water contact angle [21]. The hydrophilic surface of the electrode is one of the prime requirements in super capacitor application as there is better insertion of electrolytes within the pores of the electrode material.

**Fig. 4.9:** Contact angle images for SnO$_2$-RuO$_2$ composite films for samples, (a) C1 (5%), (b) C2 (10%), (c) C3 (15%) and (d) S4 (20%)
SECTION B: SUPERCAPACITIVE PERFORMANCE OF TIN OXIDE RUTHENIUM OXIDE COMPOSITE THIN FILMS

4.B.1 Introduction

In the present work tin oxide ruthenium oxide (SnO$_2$-RuO$_2$) composite films were used as supercapacitor electrodes. The supercapacitive performance of composite films (C1 to C4) have been studied by means of cyclic voltammetry and charge discharge study the electrode with maximum specific capacitance is found and used for further studies. The effect of electrolyte concentration, thickness of electrode material and scan rate on supercapacitive performance of optimized SnO$_2$-RuO$_2$ composite electrode is studied. The stability and electrochemical impedance studies of optimized SnO$_2$-RuO$_2$ composite are carried out.

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

The experimental details to find supercapacitive properties of SnO$_2$-RuO$_2$ composite electrodes are discussed in section 3.B.2.

4.B.3 Results and Discussion

4.B.3.1 Effect of Variation of Vol.% of RuCl$_3$ in Deposition

The cyclic voltammetry (CV) curves for SnO$_2$ and SnO$_2$-RuO$_2$ composite electrodes in the potential region between 0 to +0.8 V vs. SCE at 20 mV.s$^{-1}$ are employed to evaluate the electrochemical characteristics of the supercapacitors based on SnO$_2$-RuO$_2$ composites. The CV curve for SnO$_2$ is shown in Fig. 4.10 (a), which revealed the double layer capacitance mechanism as no redox transitions are observed in this potential region. The observed current is less compared with composite electrodes, a double layer capacitance of $\sim$ 4 F.g$^{-1}$ is observed for SnO$_2$. The CV curves for composite electrodes are shown in Fig. 4.10 (b) to (e) which shows a different type of CV nature compared with pure SnO$_2$ with the presence of redox transitions clearly confirming the pseudocapacitive mechanism. As the capacitance originating from SnO$_2$ is very small, the pseudocapacitance
coming from SnO$_2$-RuO$_2$ composite electrodes is mainly attributed to the RuO$_2$. From the curve, it is observed that the current under the curve increases with increase volume of RuCl$_3$ in the deposited bath. This may be due to the increase in volume of RuCl$_3$ in the bath it gives more number of Ru$^{3+}$ ions, which increases the content of RuO$_2$ in deposition. The increase in the RuO$_2$ content increases the current of CV curves. Therefore, specific capacitance of the composite electrode increases from 42 (sample C1) to 164 F.g$^{-1}$ (sample C3) as the volume of RuCl$_3$ in the bath increases upto 15%. The current of the CV curve for the SnO$_2$-RuO$_2$ composite increases upto 15 vol.% of RuCl$_3$. For further increment in vol.% of RuCl$_3$ in deposition (20 vol.%), there observed a decrease in the voltammetric current. From this, it is observed that 15 vol.% is the maximum limit of volume of RuCl$_3$ in the deposition bath which gives the maximum current response. The less CV response above this composition is due the decrease in the RuO$_2$ content in composite film decreasing specific capacitance to 121 F.g$^{-1}$. This can be attributed to the decrease in electroactive sites for 20 vol.% of RuCl$_3$ in the deposition bath [22].
Fig. 4.10: The CV curves of (a) SnO$_2$ and SnO$_2$-RuO$_2$ composite electrodes for samples, (b) C1 (5 vol.%), (c) C2 (10 vol.%), (d) C3 (15 vol.%), and (e) C4 (20 vol.%) in the potential range of 0 to +0.8 V vs. SCE at 20 mV.s$^{-1}$ scan rate in 0.5 M H$_2$SO$_4$.

**4.B.3.2 Charge-discharge studies**

The charge–discharge behavior of the SnO$_2$-RuO$_2$ composite electrodes (C1, C2, C3 and C4) is examined by chronopotentiometry from 0 to +0.8 V vs. SCE at the current density of 0.5 mA.cm$^{-2}$ in 0.5 M H$_2$SO$_4$ electrolyte is shown in Fig. 4.11. A nonlinear variation of potential versus time is displayed, which may be due to pseudocapacitance performance arisen from the electrochemical adsorption–desorption or redox reaction at an interface between the electrode and the electrolyte [23]. Fig. 4.12 shows Ragone plot relating power density to achievable energy density. From the plot, it is observed that the observed values of energy density and power density of composite electrodes are according to Ragone plot.
typically calculated for supercapacitors [24]. From the plot, it is observed that composite C3 has maximum energy density of 9.8 Wh.kg$^{-1}$ at still high power density of 0.84 kW.kg$^{-1}$. As the energy density is dependent on the value of discharging time, the high energy density observed is due to the large discharging time of the SnO$_2$-RuO$_2$ composite electrode (sample C3).

**Fig. 4.11:** The charge-discharge curves of SnO$_2$-RuO$_2$ composite electrodes for samples, (a) C1 (5 vol.%), (b) C2 (10 vol.%), (c) C3 (15 vol.%), and (d) C4 (20 vol.%), in the potential range of 0 to +0.8 V vs. SCE at the current density of 0.5 mA.cm$^{-2}$ in 0.5 M H$_2$SO$_4$. 


Fig. 4.12: The Ragone plot for SnO$_2$-RuO$_2$ composite electrode for samples, (a) C1 (5 vol.%), (b) C2 (10 vol.%), (c) C3 (15 vol.%), and (d) C4 (20 vol.%).

4.B.3.3 Effect of Electrolyte Concentration

The important factor to be considered is whether the capacitance is a contribution from the pseudocapacitance or the double layer capacitance at the electrode electrolyte interface. The origin of capacitance can be checked by varying the electrolyte concentration. If the capacitance originated is due to double layer contribution where the charge storage is mainly in the electrolyte, the change in the electrolyte concentration will have a direct effect on the capacitance value. If it is not the case, then there will be no variation in the capacitance of the material [25]. The effect of electrolyte concentration on the CV performance of SnO$_2$-RuO$_2$ composite electrode (sample C3) was studied by keeping the potential range and scan rate of CV constant and varying the concentration of H$_2$SO$_4$ electrolyte.
from 0.1 to 1 M. Fig. 4.13 (a) shows the CV curves for SnO$_2$-RuO$_2$ composite electrode with varying concentration of H$_2$SO$_4$ electrolyte. From the curves, it is observed that the current under the curve increases slowly with increase in concentration of H$_2$SO$_4$ electrolyte. Fig. 4.13 (b) shows the variation of specific capacitance with the electrolyte concentration. From which it is observed that increase in specific capacitance is not much affected by varying the electrolyte concentration, which means the origin of capacitance is purely of pseudocapacitive type.

**Fig. 4.13 (a):** CV curves of SnO$_2$-RuO$_2$ composite electrode (sample C3) in different H$_2$SO$_4$ concentrations at 20 mV.s$^{-1}$ scan rate.
CHAPTER-IV: SYNTHESIS AND CHARACTERIZATION OF TIN OXIDE RUTHENIUM OXIDE COMPOSITE THIN FILMS BY CHEMICAL BATH DEPOSITION (CBD) METHOD AND THEIR SUPERCAPACITIVE PERFORMANCE

**Fig. 4.13 (b):** The variation of specific capacitance of SnO$_2$-RuO$_2$ composite electrode (sample C3) with concentration of H$_2$SO$_4$.

### 4.3.4 Effect of Film Thickness

The effect of thickness of SnO$_2$-RuO$_2$ composite electrode on the capacitive behavior was studied in 0.5 M H$_2$SO$_4$ electrolyte at 20 mV.s$^{-1}$ scan rate. The thickness of SnO$_2$-RuO$_2$ composite (sample S3) is varied by varying the time for deposition. 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$^{-2}$). Fig. 4.14 (a) shows the variation in CV curves with deposited weight of electrode. From the CV curves, it is observed that the current under the curve increases with increase in deposited weight from 0.125 to 0.475 mg.cm$^{-2}$ above which with increase in deposited weight decrease in current response is observed. This means that with increase in deposited weight upto 0.475 mg.cm$^{-2}$ voltammetric charges also increased. Fig. 4.14
(b) shows the variation of interfacial and specific capacitance with deposited mass. The interfacial capacitance increased from 0.0327 to 0.607 F.cm\(^{-2}\) with increase in deposited weight up to the critical value of deposited weight (0.475 mg.cm\(^{-2}\)), after that decrease in interfacial capacitance is observed which may be due the less number of voltammetric charges. The specific capacitance decreased from 262 to 127 F.g\(^{-1}\) with increase in deposited weight. Similar type of trend of decreasing specific capacitance with increasing deposited weight has been observed by park et. al. [26] and Gujar et. al. [27].

![Graph showing CV curves with deposited weight of SnO\(_2\)-RuO\(_2\) composite electrode (sample C3) in 0.5 M H\(_2\)SO\(_4\) electrolyte in the potential range of 0 to +0.8 V vs. SCE at 20 mV.s\(^{-1}\).](image)

**Fig. 4.14 (a):** The variation of CV curves with deposited weight of SnO\(_2\)-RuO\(_2\) composite electrode (sample C3) in 0.5 M H\(_2\)SO\(_4\) electrolyte in the potential range of 0 to +0.8 V vs. SCE at 20 mV.s\(^{-1}\).
Fig. 4.14 (b): The variation of interfacial and specific capacitance of SnO$_2$-RuO$_2$ composite electrode (sample C3) with weight deposited.

4.B.3.5 Effect of Scan Rate

Fig. 4.15 (a) shows the effect of scan rate on SnO$_2$-RuO$_2$ composite electrode with 0.475 mg.cm$^{-2}$ film thickness. It is observed that the current increased linearly with scan rate, and rectangular shape of the CV curve maintained at high scan rate indicating the good power properties of electrode. Fig. 4.15 (b) shows the variation of interfacial and specific capacitances with the scan rate. From the graph, it is seen that the interfacial and specific capacitances are decreased from 0.075 F.cm$^{-2}$ and 157 F.g$^{-1}$ to 0.027 F.cm$^{-2}$ and 58 F.g$^{-1}$, 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
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 [28].

**Fig. 4.15 (a):** The CV curves of SnO$_2$-RuO$_2$ composite electrode (sample C3) at different scan rates in 0.5 M H$_2$SO$_4$ electrolyte.
4.B.3.6 Stability Studies

Stability of SnO$_2$-RuO$_2$ composite electrode (0.475 mg.cm$^{-2}$) in 0.5 M H$_2$SO$_4$ electrolyte was tested by CV. Fig. 4.16 (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 to +0.8 V vs. SCE, after different number of cycles. It is found that the current under the curve decreased after 2000 cycles, above which there negligible loss in the current (not shown). The decrease in specific capacitance with different cycle numbers is shown in Fig. 4.16 (b). The specific capacitance decreased from 67 to 59 F.g$^{-1}$ with increasing in cycle numbers to 2000 cycles. The capacitance retained ratio after 2000
cycles is 88% showing the stable nature of SnO$_2$-RuO$_2$ composite electrode useful in supercapacitor application.

**Fig. 4.16 (a):** CV curves for SnO$_2$-RuO$_2$ composite electrode (sample C3) at various cycle numbers in 0.5 M H$_2$SO$_4$ electrolyte at 100 mV.s$^{-1}$ scan rate.
**Fig. 4.16 (b):** The variation of specific capacitance of SnO$_2$-RuO$_2$ composite (sample C3) at various cycle numbers in 0.5 M H$_2$SO$_4$.

**4.B.3.7 Electrochemical Impedance Analysis**

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 C3) was carried out in 0.5 M H$_2$SO$_4$. The Nyquist depictions ($Z'$ vs. $Z''$) of the raw impedance data is shown in Fig. 4.17. For the convenience of the interpretation, this plot can be divided into high and low frequency regions. In the high frequency range, the intercept at real part ($Z'$) is a combinational resistance of ionic resistance of electrolyte, intrinsic resistance of substrate, and contact resistance between the active material and the current collector [31]. 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 $\sim 45^0$ to the real
axis is attributed to the capacitive behavior. Inset (Fig. 4.17) 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 high frequency impedance intercept of 12 Ω, reflects the equivalent series resistance (ESR) of the electrolyte.

Fig. 4.18 shows the Bode plot (phase angle (Φ) vs. frequency) at a phase angles of 20 and 72° about 94% and 31% of the powers corresponds to heat production at the internal resistance with a loss factor of electrode 2.7 and 0.32 are calculated in the higher and lower frequency regions, respectively. The relaxation time constant ($\tau_0$), calculated from fig. 4.19 (plot of $C'$ vs. frequency) for the sample C3 is 0.7 s. The Small relaxation time constant $\tau_0$ value exhibits a fast energy release capability of the electrode to provide higher power density, which decides applicability of electrode material according to energy demand. [33].
**Fig. 4.17**: Nyquist plot of SnO$_2$-RuO$_2$ composite electrode (sample C3) in 0.5 M H$_2$SO$_4$. 
Fig. 4.18: Bode plot of SnO$_2$-RuO$_2$ composite electrode (sample C3) in 0.5 M H$_2$SO$_4$. 
Fig. 4.19: Plot of real capacitance ($C'$) vs. frequency for SnO$_2$-RuO$_2$ composite electrode (sample C3).

**Conclusions**

In conclusion, amorphous SnO$_2$-RuO$_2$ composite films have been prepared by varying volume of RuCl$_3$ in the deposition bath using CBD method. As revealed from CV studies, a maximum specific capacitance of 262 F.g$^{-1}$ is observed for the SnO$_2$-RuO$_2$ composite film with 15 vol% of RuCl$_3$ in the deposition bath with 0.125 mg.cm$^{-2}$ electrode thickness. This means that the CBD method is useful for depositing SnO$_2$-RuO$_2$ with minimum uses of RuCl$_3$ precursor and optimum specific capacitance value. The capacitance retained ratio after 2000 cycles is 88% proved the stable nature of SnO$_2$-RuO$_2$ composite electrode. The specific energy of 9.8 Wh.kg$^{-1}$ with specific power of 0.84 kW.kg$^{-1}$ observed for SnO$_2$-RuO$_2$ composite makes it promising electrode in supercapacitor application.
References


